— SECTION B —

CHEMICAL SCIENCES

Contents

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β-AMINOETHYLCARBAZOLES[1]

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Abstract

1-, 2-, 3-, and 4-Acetylcarbazoles were converted to the corresponding carba-zolylacetamides by the Willgerodt reaction. These were dehydrated with phosphorus oxychloride and the resulting 1-, 2-, 3-, and 4-cyanomethylcarbazoles reduced catalytically to the corresponding β-aminoethylcarbazoles. The syntheses of 1- and 4-acetylcarbazoles and 1-methoxy-4-β-aminoethyl-5, 6, 7, 8-tetrahydrocarbazole are described.

The purpose of this investigation was to synthesize the heretofore unknown 1-, 2-, 3-, and 4-β-aminoethylcarbazoles*, which were required in connection with another problem. Suitable starting materials for this work were the corresponding acetylcarbazoles, preparative methods for two of which, namely, 2- (3) and 3-acetylcarbazoles (12) were reported. 1-Acetylcarbazole (III) was prepared from 1-carbazolecarboxylic acid (I) (1, 6, 4) by conversion to the acid chloride (II) with thionyl chloride in chloroform and treatment of II with zinc dimethyl (5, 14).

$$\text{RCOOH} \longrightarrow \text{RCOCl} \xrightarrow{\text{Zn(CH}_3)_2} \text{RCOCH}_3 \quad R^* =$$

$$\text{(I)} \qquad\qquad \text{(II)} \qquad\qquad \text{(III)}$$
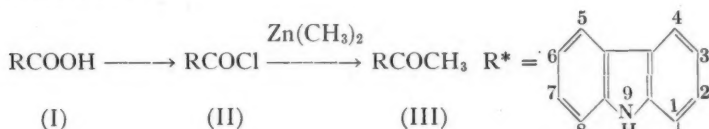
4-Acetylcarbazole (VII) was prepared according to the following series of reactions:

(IV)   (V)   (VI)   (VII)
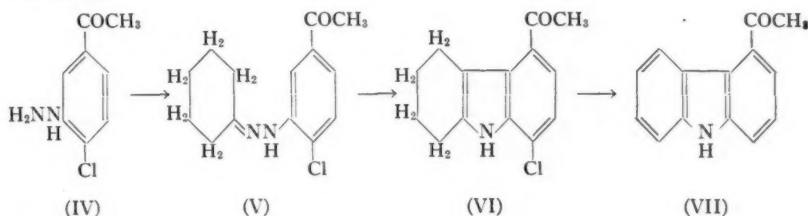
3-Amino-4-chloroacetophenone (11) was diazotized and the diazonium salt reduced to the hydrazine (IV). This without purification was treated with

cyclohexanone and the resulting crude hydrazone (V) which contained some condensate of the hydrazine (IV) and the ketone (V) was cyclized with dilute sulphuric acid to 1-chloro-4-acetyl-5, 6, 7, 8-tetrahydrocarbazole (VI).   The over-all yield of VI based on 3-amino-4-chloroacetophenone was 38%.   Simultaneous dehydrogenation and dechlorination of VI to 4-acetylcarbazole (VII) was achieved in 80% yield by heating under reflux in a solution of tetralin and naphthalene in the presence of platinum catalyst for 21 days.

An attempt to prepare 1-acetylcarbazole (III) from o-aminoacetophenone in a manner similar to that described above for VII did not succeed, the only product of the reaction being the acid-soluble 3-methylindazole (9).

The 1-, 2-, 3-, and 4-acetylcarbazoles (VIII) were converted to the corresponding β-aminoethylcarbazoles (XI) according to the following reactions:

$$RCOCH_3 \longrightarrow RCH_2CONH_2 \longrightarrow RCH_2CN \longrightarrow RCH_2CH_2NH_2$$
$$\text{(VIII)} \qquad\qquad \text{(IX)} \qquad\qquad \text{(X)} \qquad\qquad \text{(XI)}$$
$$\downarrow \qquad\qquad\qquad \downarrow$$
$$RCH_2CH_3 \qquad\quad RCH_2COOH \qquad R = \text{1-, 2-, 3- and 4-carbazolyl .}$$
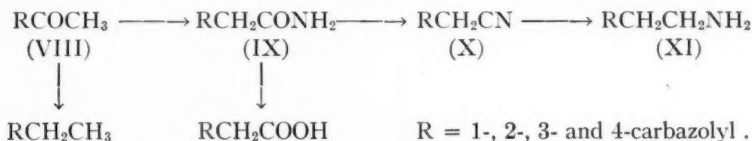
The acetylcarbazoles (VIII) reacted readily with ammonium polysulphide according to the method of Gilman and Avakian (10) to give the corresponding carbazolylacetamides (IX).   An alternate route to 1-carbazolylacetamide was the treatment of 1-carbazolecarboxylic acid chloride (II) with diazomethane followed by the Arndt–Eistert rearrangement of the resulting 1-carbazolyl diazomethyl ketone.   The carbazolylacetamides (IX) were dehydrated to the cyanomethylcarbazoles (X) using phosphorus oxychloride and a short reaction time.   These compounds (IX) and especially 1- and 4-carbazolylacetamides react with phosphorus oxychloride in an unknown manner when heating is prolonged, and very little of the cyanomethylcarbazoles are formed. The conversion of the cyanomethylcarbazoles (X) to the corresponding β-aminoethylcarbazoles (XI) was accomplished by hydrogenation in the presence of Raney nickel catalyst and ammonia.

In these series of substituted carbazoles there seems to be a relationship between their properties and the position of the substituent.   With few exceptions the melting points of carbazoles carrying the same substituent in different positions decrease in the order of 2-, 3-, 4-, and 1.   The solubilities increase in the same order of substitution.   Most 2-substituted carbazoles are only difficultly soluble in organic solvents, and the hydrochloride of 2-β-aminoethylcarbazole is extremely insoluble in hot water.

In an unsuccessful attempt to synthesize 4-β-aminoethylcarbazole by an alternate route, 1-methoxy-4-β-aminoethyl-5, 6, 7, 8-tetrahydrocarbazole was prepared but it could not be dehydrogenated nor demethoxylated.   3-Nitro-4-methoxybenzyl chloride (8) freed from bis(3-methoxy-4-nitrophenyl)methane (13) by distillation was treated with potassium cyanide and the resulting

3-nitro-4-methoxybenzyl cyanide (7) reduced with stannous chloride to 3-amino-4-methoxybenzyl cyanide. This was diazotized and the diazonium salt reduced to 3-hydrazino-4-methoxybenzyl cyanide. The latter formed a hydrazone with cyclohexanone which underwent the Fischer indole ring closure in the presence of acid to 1-methoxy-4-cyanomethyl-5, 6, 7, 8-tetrahydro-carbazole. Catalytic reduction gave the required 1-methoxy-4-β-aminoethyl-5, 6, 7, 8-tetrahydrocarbazole.

Experimental

2-Acetylcarbazole (3)

To N-acetylcarbazole (2) (20 gm.), acetyl chloride (25 gm.) and carbon disulphide (100 cc.) was added aluminum chloride (50 gm.) with cooling and then the reaction mixture stirred and heated under reflux for three hours. The bottom viscous layer was separated and added cautiously to cracked ice. The resulting solid was filtered, washed with water, and crystallized from ethanol; yield of 2,N-diacetylcarbazole, 15.5 gm., m.p. 106° to 107°C.* Literature (3), 104°C. This was hydrolyzed by heating with 20% sulphuric acid (10 cc.) and ethanol (100 cc.) under reflux for one hour and crystallized from toluene, yield 12.0 gm., m.p. 230° to 231°C.

1-Acetylcarbazole

1-Carboxycarbazole (1, 4, 6) (7.5 gm.) was suspended in dry chloroform (200 cc.), thionyl chloride (15 cc.) added, and the reaction mixture heated under reflux until solution was complete (about 2½ hr.). The solution was concentrated to 50 cc., cooled, filtered, and washed with cold chloroform. The yield of *1-carbazolecarboxylic acid chloride* in two successive crops was 7.8 gm., m.p. 179° to 180°C., crystallized from benzene, yellow needles, m.p. 179° to 180°C. Calc. for $C_{13}H_8NOCl$: C, 67.97; H, 3.49; N, 6.10%. Found: C, 67.83, 67.81; H, 3.37, 3.38; N, 6.06%.

To zinc dimethyl (5, 14) (3 gm.) in dry toluene (65 cc.) cooled to 0°C. was added 1-carbazolecarboxylic acid chloride (3.5 gm.), and the reaction mixture stirred for ¼ hr. and then heated on the steam bath for 1½ hr. The dark cooled reaction mixture was washed with dilute sulphuric acid, with sodium hydroxide solution, and with water, and then the solvent was removed. The residue was distilled from a Späth bulb, b.p. (1 mm.) about 200°C., and the distillate (2.3 gm.) crystallized from methanol twice; yield, 1.8 gm. or 60%, m.p. 133° to 134°C. Literature (12), 136°C.

1-Ethylcarbazole

To a solution of 1-acetylcarbazole (0.2 gm.) in ethylene glycol (25 cc.) was added hydrazine hydrate (0.5 cc.), and then about 5 cc. of liquid was distilled off from this solution in order to remove the excess hydrazine and the water. Potassium hydroxide (0.5 gm.) was added to the cooled solution and the re-

All melting points are corrected.

sulting solution heated under reflux for four hours. This was taken almost to dryness, water was added to the residue and then the aqueous mixture was extracted with ether. The ether was removed and the residual oil distilled, b.p. (3 mm.) about 200°C. The colorless distillate (0.10 gm.) which solidified on standing was crystallized from petroleum ether (30° to 50°C.), m.p. 73 to 74°C. Calc. for $C_{14}H_{13}N$: C, 86.16; H, 6.67; N, 7.18%. Found: C, 85.68, 85.79; H, 6.42, 6.43; N, 7.05%.

1-Chloro-4-acetyl-5, 6, 7, 8-tetrahydrocarbazole (VI)

3-Amino-4-chloroacetophenone (11) (40 gm.) in water (500 cc.) and concentrated hydrochloric acid (60 cc.) was cooled and diazotized at −1°C. with a solution of sodium nitrite (16.0 gm.) in water (100 cc.). After standing at −1°C. for an additional 15 min. the reaction mixture was added portionwise to stirred and cooled stannous chloride dihydrate (140 gm.) in concentrated hydrochloric acid (200 cc.) over a period of about 10 min. The temperature was not allowed to go over 10°C. The resulting reaction mixture was stirred at 5° to 10°C. for one hour and then added to 20% sodium hydroxide (1600 cc.) and ice (1600 gm.) with stirring. The hydrazine IV was then extracted with three 2 liter portions of ether. To the combined extracts was added cyclohexanone (80 cc.), and the solution allowed to stand for two days and the ether distilled off. When methanol (100 cc.) was added to the oily hydrazone a small quantity of orange prisms separated which when crystallized from ethanol melted at 171° to 173°C. and analyzed for the condensate of two moles of 3-hydrazino-4-chloroacetophenone and one mole of cyclohexanone or the *condensate of the ketone V and the hydrazine IV*. Calc. for $C_{22}H_{24}N_4Cl_2O$: C, 61.25; H, 5.56; N, 12.98%. Found: C, 61.19, 61.10; H, 5.62, 5.52; N, 12.80%.

To the methanol solution of the crude hydrazone V was added 17% sulphuric acid (300 cc.) and the reaction mixture heated in an open flask on the steam bath for four hours. The tarry material which separated was extracted with ether, the solvent removed, and the residue distilled, b.p. (1 mm.) about 210°C. The distillate (28 gm.) was crystallized from methanol, yield of the light-yellow VI in two successive crops was 22 gm. or 38%, m.p. 162° to 163°C. Calc. for $C_{14}H_{14}ONCl$: C, 67.87; H, 5.65; N, 5.65%. Found: C, 68.21; 68.02; H, 5.49, 5.33; N, 5.68%.

4-Acetylcarbazole (VII)

1-Chloro-4-acetyl-5, 6, 7, 8-tetrahydrocarbazole (VI) (20 gm.), tetralin (1 liter), distilled naphthalene (50 gm.), and Adams' platinum catalyst (1.0 gm.) were heated under reflux in an atmosphere of nitrogen until no more hydrogen chloride was liberated (*about 21 days*). The catalyst was filtered, the tetralin and naphthalene distilled off under reduced pressure, and the residue distilled, b.p. (1 mm.) about 210°C., crystallized from methanol, light-yellow plates, m.p. 161° to 162° C., yield, 14 gm. or 80%. Calc. for $C_{14}H_{11}ON$: C, 80.39; H, 5.26; N, 6.70%. Found: C, 80.55, 80.30; H, 5.20, 5.03: N, 6.39%.

4-Ethylcarbazole

The 4-acetylcarbazole was reduced by the method of Wolff–Kishner as described above for 1-ethylcarbazole; yield, 75%, white needles, m.p. 72° to 73°C. Calc. for $C_{14}H_{13}N$: C, 86.16; H, 6.67; N, 7.18%. Found: C, 86.09, 86.17; H, 6.57, 6.39; N, 7.23%.

1-Carbazolylacetamide (IX)

(a) *From 1-carbazolecarboxylic acid chloride*

To 1-carbazolecarboxylic acid chloride (II) (8.0 gm.) suspended in dry ether (300 cc.) was added a diazomethane solution in ether (400 cc.) (from 24 gm. nitrosomethyl urea), and the reaction mixture stirred and cooled for a few minutes and then allowed to stand at room temperature overnight. The yellow solution was filtered and the ether distilled off from the filtrate. The residual *1-carbazolyl diazomethyl ketone* melted at 155° to 157°C. with decomposition. A small portion was purified by crystallization from benzene; golden needles, m.p. 156° to 157°C. (with decomposition). Calc. for $C_{14}H_9ON_3$: C, 71.48; H, 3.83%. Found: C, 70.84, 70.95; H, 4.09, 3.89%.

The crude 1-carbazolyl diazomethyl ketone was dissolved in dioxane (200 cc.) heated up to 75°C., a solution of silver nitrate (1.0 gm.) in 2 cc. water and concentrated ammonium hydroxide (40 cc.) added, and the reaction mixture heated under reflux for four hours. The silver oxide was filtered and the filtrate taken to dryness under reduced pressure. The residual tar was stirred and warmed with benzene (25 cc.) and then cooled. The precipitate was filtered and crystallized from methanol or benzene; fine white needles, m.p. 203° to 204° C., yield 2.3 gm. or 30%. Calc. for $C_{14}H_{12}N_2O$: C, 75.00; H, 5.36; N, 12.50%. Found: C, 75.09, 75.45; H, 5.19, 5.29; N, 12.53%.

(b) *From 1-acetylcarbazole*

Into concentrated ammonium hydroxide (20 cc.) and sulphur (2.0 gm.), hydrogen sulphide was passed until all the sulphur dissolved. To this was added 1-acetylcarbazole (2.0 gm.) and dioxane (8 cc.) and the reaction mixture heated in a sealed bomb at 150°C. for eight hours. The red solution was cooled to 0°C. The precipitated 1-carbazolylacetamide (1.3 gm. or 60%) was filtered, washed with dilute ammonium sulphide and with water, and dried; m.p. 203° to 204°C. either alone or in admixture with that obtained in (a).

1-Carbazolylacetic acid

To a solution of 1-carbazolylacetamide (0.15 gm.) in ethanol (50 cc.) was added a hot solution of potassium hydroxide (3 gm.) in water (25 cc.) and the resulting solution heated under reflux for seven hours. The ethanol was distilled off, the aqueous solution filtered, and the filtrate acidified. The white precipitate (0.14 gm.) was filtered, washed with water, dried, and crystallized from benzene; white plates, m.p. 211° to 212°C. Calc. for $C_{14}H_{11}NO_2$: C, 74.66; H, 4.89; N, 6.22%. Found: C, 74.31, 74.51; H, 4.89, 4.73; N, 6.30%.

4-Carbazolylacetamide (IX)

This was prepared from 4-acetylcarbazole, following the same directions as described for 1-carbazolylacetamide (b); yield 67%, crystallized from methanol or acetone, light-yellow needles, m.p. 206° to 207°C. Calc. for $C_{14}H_{12}N_2O$: C, 75.00; H, 5.36; N, 12.50%. Found: C, 74.75, 75.07; H, 5.22, 5.27; N, 12.55%.

4-Carbazolylacetic acid

4-Carbazolylacetamide was hydrolyzed in the same manner as was 1-carbazolylacetamide (see above); yield almost quantitative, small white prisms from benzene, m.p. 181° to 182°C. Calc. for $C_{14}H_{11}NO_2$: C, 74.66; H, 4.89; N, 6.22%. Found: C, 74.78, 74.67; H, 4.59, 4.73; N, 6.21%.

1-Cyanomethylcarbazole (X)

To a solution of dry chloroform (50 cc.) and phosphorus oxychloride (5 cc.) was added 1-carbazolylacetamide (1.5 gm.) and the reaction mixture heated under reflux for one hour. The solvent was removed under slightly reduced pressure, to the residue warm water was added, and the sticky cyanomethyl compound pulverized, filtered, washed, and distilled from a Späth bulb, b.p. (1 mm.) about 200°C. The distillate was crystallized from benzene and from ethanol; dried, white prisms (1.0 gm. or 70%), m.p. 147° to 148°C. Calc. for $C_{14}H_{10}N_2$: C, 81.56; H, 4.85; N, 13.59%. Found: C, 81.44, 81.06; H, 4.60, 4.95; N, 13.65%. In another experiment when the 1-carbazolylacetamide was added to excess phosphorus oxychloride and *no chloroform* and the reaction mixture warmed, a violent reaction took place giving a resinous material from which only a small quantity of the 1-cyanomethylcarbazole could be isolated.

4-Cyanomethylcarbazole (X)

To 4-carbazolylacetamide (2.3 gm.) was added phosphorus oxychloride (25 cc.) and the reaction mixture heated on the steam bath for 15 min. (longer heating reduces the yield). The excess phosphorus oxychloride was distilled off under reduced pressure and the residual crude 4-cyanomethylcarbazole worked up as described above; yield 66%, white needles from benzene (dried *in vacuo*), m.p. 144° to 145°C. Calc. for $C_{14}H_{10}N_2$: C, 81.56; H, 4.85; N, 13.59%. Found: C, 81.56, 82.01; H, 4.79, 4.60; N, 13.29%.

2-Cyanomethylcarbazole (X)

This was prepared from 2-carbazolylacetamide (10) (m.p. 296°C.) by either of the methods described above for 1- and 4-cyanomethylcarbazole; yield 58%, white needles from ethanol or benzene, m.p. 193° to 194°C. Calc. for $C_{14}H_{10}N_2$: C, 81.56; H, 4.85; N, 13.59%. Found: C, 82.13, 81.98; H, 5.15, 4.97; N, 13.33%.

3-Cyanomethylcarbazole (X)

This was prepared from 3-carbazolylacetamide (10) (m.p. 236°C.) in the same manner as was 4-cyanomethylcarbazole above; yield 58%, white needles from benzene and ethanol, m.p. 168° to 169°C. Calc. for $C_{14}H_{10}N_2$: C, 81.56; H, 4.85; N, 13.59%. Found: C, 81.72, 82.25; H, 4.83, 5.10; N, 13.21%.

3-Cyanomethyl-9-acetylcarbazole

3-Cyanomethylcarbazole (0.5 gm.) was dissolved in acetic anhydride (7 cc.), one drop of concentrated sulphuric acid added, and the solution heated on the steam bath for $\frac{1}{2}$ hr. The reaction mixture was poured into cold water, stirred, and the white precipitate filtered, washed, dried, and crystallized from benzene, m.p. 127° to 128°C.; yield of colorless needles, 0.35 gm. Calc. for $C_{16}H_{12}N_2O$: C, 77.41; H, 4.84; N, 11.29%. Found: C, 77.43, 77.48; H, 4.77, 4.66; N, 11.00%.

1-β-Aminoethylcarbazole (XI)

To methanol saturated with ammonia gas (100 cc.) was added 1-cyano-methylcarbazole (0.80 gm.) and Raney nickel catalyst (about 2 gm.) and the reaction mixture shaken under 45 lb. of hydrogen for 18 hr. The catalyst and solvent were removed, the residue extracted with dilute hydrochloric acid, filtered, and the filtrate basified with sodium hydroxide solution. The precipitate was filtered, washed, dried, and distilled from a Späth bulb, b.p. (1 mm.) about 210°C. The colorless distillate which soon solidified was crystallized from benzene; colorless prisms, m.p. 109° to 110°C., yield, 0.28 gm. Calc. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.67; N, 13.33%. Found: C, 80.12, 79.93; H, 6.60, 6.48; N, 13.36%.

4-β-Aminoethylcarbazole (XI)

4-Cyanomethylcarbazole was reduced in the same manner as was 1-cyano-methylcarbazole above; yield 75%, microscopic white needles from benzene, m.p. 150° to 152°C. Calc. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.67; N, 13.33%. Found: C, 80.21, 79.90; H, 6.18, 6.15; N, 13.56%.

3-β-Aminoethylcarbazole (XI)

3-Cyanomethylcarbazole was reduced in the same manner as was 1-cyano-methylcarbazole above; yield 85%, colorless needles from benzene, m.p. 153° to 154°C. Calc. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.67; N, 13.33%. Found: C, 80.29, 80.40; H, 6.52, 6.71; N, 13.10%.

2-β-Aminoethylcarbazole (XI)

2-Cyanomethylcarbazole could *not* be reduced by the same method as was 1-cyanomethylcarbazole because it is not soluble in cold methanolic-ammonia solution.

To ethanol saturated with ammonia (300 cc.) was added 2-cyanomethyl-carbazole (10 gm.) and Raney nickel catalyst (about 10 gm.). The reaction mixture was then hydrogenated at 115° under 2000 lb. hydrogen pressure for eighteen hours. The catalyst and solvent were removed and the residue distilled, b.p. (0.3 mm.) about 200°C. The distillate was crystallized from methanol and benzene; fine white needles, m.p. 179° to 180°C., yield 60%. Calc. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.67; N, 13.33%. Found: C, 80.09, 80.29; H, 6.64, 6.55; N, 13.29%. This amine was not soluble in dilute mineral acids.

4-Methoxy-3-nitrobenzyl cyanide (7)

To a hot solution of *distilled** 3-nitro-4-methoxybenzyl chloride (8) (48 gm.) in ethanol (300 cc.) was added a solution of potassium cyanide (20 gm.) in water (50 cc.), and the reaction mixture heated under reflux for two hours. This was added to cold water (1.5 liter), and the precipitate filtered, washed, dried, and distilled, b.p. (3 mm.) = 180° to 190°C. The distillate (34 gm.) was crystallized from methanol; light-yellow prisms, m.p. 86° to 87°C., yield 30 gm. or 65%. Calc. for $C_9H_8N_2O_3$: C, 56.24; H, 4.17; N, 14.58%. Found: C, 56.40, 56.46; H, 4.26, 4.22; N, 14.27%.

4-Methoxy-3-aminobenzyl Cyanide

A solution of 4-methoxy-3-nitrobenzyl cyanide (25 gm.) in glacial acetic acid (75 cc.) was added dropwise to stirred stannous chloride dihydrate (120 gm.) in concentrated hydrochloric acid (100 cc.) over a period of about 10 min., the temperature being kept below 30°C. by cooling. The reaction mixture was stirred at 30° to 35°C. for 2.5 hr. (occasional cooling was necessary) and then poured into chilled 15% sodium hydroxide solution (1 liter) with cooling. The amine was extracted with three 350 cc. portions of ether, the solvent removed from the extract, and the residue distilled; b.p. (3 mm.) = 153° to 155°C., yield 19.2 gm. or 90%. The distillate solidified on cooling and melted at 40° to 41°C.; crystallized from benzene–petroleum ether, white needles, m.p. 42° to 43°C. Calc. for $C_9H_{10}N_2O$: C, 66.66; H, 6.17; N, 17.29%. Found: C, 66.77, 66.95; H, 5.95, 6.07; N, 16.86%.

3-Hydrazino-4-methoxybenzyl Cyanide

3-Amino-4-methoxybenzyl cyanide (16.5 gm.) in glacial acetic acid (80 cc.) and concentrated hydrochloric acid (33 cc.) was diazotized at 3°C. with a solution of sodium nitrite (7.0 gm.) in water (50 cc.) and the diazonium salt solution added as quickly as possible to a stirred solution of stannous chloride dihydrate (80 gm.) in concentrated hydrochloric acid (80 cc.), the temperature being maintained at 5° to 10°C. by cooling. After allowing to stand for 15 min. the thick slurry was added to 10% sodium hydroxide (2 liters) with

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*3-Nitro-4-methoxybenzyl chloride cannot be separated from bis(3-nitro-4-methoxyphenyl)methane (13) by crystallization. The treatment of impure 3-nitro-4-methoxybenzyl chloride with potassium cyanide yields a product which decomposes violently when heated.

cooling and stirring. The hydrazine was extracted with four 300 cc. portions of ether, and the ether extract concentrated and cooled. The light-brown prisms (6.9 gm. or 40%) were filtered and dried, m.p. 68° to 69°C. Calc. for $C_9H_{11}ON_3$: C, 61.02; H, 6.21; N, 23.72%. Found: C, 61.14, 61.34; H, 6.13, 6.27; N, 23.52, 23.79%.

The Hydrazone of 3-Hydrazino-4-methoxybenzyl Cyanide and Cyclohexanone

To 3-hydrazino-4-methoxybenzyl cyanide (5.5 gm.) dissolved in methanol (20 cc.) was added cyclohexanone (3.0 gm.) and the solution allowed to stand at room temperature for two hours. The precipitated white needles (7.2 gm. or 90%) were filtered, washed with methanol, and dried, m.p. 106° to 107°C. Calc. for $C_{15}H_{19}N_3O$: C, 70.05; H, 7.40; N, 16.34%. Found: C, 70.14, 69.87; H, 7.27, 7.38; N, 16.10, 16.42%.

1-Methoxy-4-cyanomethyl-5, 6, 7, 8-tetrahydrocarbazole

To a hot solution of the hydrazone (7.2 gm.) of 3-hydrazino-4-methoxybenzyl cyanide and cyclohexanone in glacial acetic acid (50 cc.) was added concentrated hydrochloric acid (2.1 cc.) and the solution heated on the steam bath for five minutes. The dark reaction mixture was poured into cold water (200 cc.) with stirring and the brown precipitate filtered, washed, dried, and distilled from a Späth bulb, b.p. (0.5 mm.) about 200°C. The distillate (2.5 gm.) was crystallized from methanol, yielding colorless needles (1.8 gm. or 30%), m.p. 178° to 179°C. Calc. for $C_{15}H_{16}N_2O$: C, 75.00; H, 6.66; N, 11.67%. Found: C, 74.50, 74.58; H, 6.48, 6.51; N, 12.07, 11.44%.

1-Methoxy-4-β-aminoethyl-5, 6, 7, 8-tetrahydrocarbazole

The 1-methoxy-4-cyanomethyl-5, 6, 7, 8-tetrahydrocarbazole was reduced in the same manner as was 1-cyanomethylcarbazole above; yield 70%, colorless prisms from ether, m.p. 114° to 115°C. Calc. for $C_{15}H_{20}N_2O$: C, 73.77; H, 8.20; N, 11.47%. Found: C, 73.90, 73.55; H, 7.95, 8.01; N, 11.16%.

1-Methoxy-4-phthalimidoethyl-5, 6, 7, 8-tetrahydrocarbazole was prepared by heating 1-methoxy-4-β-aminoethyl-5, 6, 7, 8-tetrahydrocarbazole with phthalic anhydride at 230°C. for 10 min. The cooled cake was crystallized from acetone and methanol; yellow needles, m.p. 233 to 234°C. Calc. for $C_{23}H_{22}O_3N_2$: C, 73.80; H, 5.88; N, 7.49%. Found: C, 73.77, 73.57; H, 6.15, 5.91; N, 7.33%.

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SYNTHESIS OF LARGE RING DIENES AND THEIR REACTION WITH MALEIC ANHYDRIDE[1]

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Abstract

Cyclotetradecanol–on–2 was dehydrated in the gas phase to cyclotetradecen-one–3. The latter was reduced with lithium aluminum hydride to cyclotetra-decen–ol–3, which was converted by dehydration to cyclotetradecadiene. This compound gave with maleic anhydride 3-6-decamethylene tetrahydrophthallic anhydride. The same series of reactions was performed in the cycloöctadecane series.

V. Prelog and K. Wiesner (3) have shown that polymethylene bridges in the meta position of the benzene ring can be constructed by starting with a preformed large ring and building the benzene ring by a condensation reaction. They treated large ring ketones with the sodium salt of nitromalonic dialdehyde and obtained a series of homologous 2-6-polymethylene-4 nitrophenols. Although the smallest bridge prepared up to this time by Luttringhaus (1) contained 9 atoms (resorcin heptamethylene ether) it was possible to prepare the nitrophenols with a 5 and 6 membered bridge. While the hexamethylene nitrophenol exhibited normal properties, the pentamethylene compound was shown to react in a tautomeric form because of the strain.

In order to devise a synthetic approach to compounds with a polymethylene bridge in the para position, starting from a preformed large ring, we investigated the synthesis of large ring dienes and their Diels–Alder reactions.

Our starting materials were the cyclic acyloins I($n = 14$, $n = 18$) prepared according to the directions of V. Prelog, L. Frenkiel, M. Kobelt, and P. Barman (2).

M. Stoll (5) has distilled cyclohexadecadiol II($n = 16$) through a heated alumina column and obtained a mixture of cyclohexadecanone and a smaller amount of a hydrocarbon which he claimed to be cyclohexadecadiene.

We decided to try first this approach to the synthesis of our dienes.

We have reduced our 14 and 18 membered ring acyloins to the as yet unreported cyclotetradeca and cycloöctadeca diols II($n = 14$, $n = 18$). This reduction can be performed by means of platinum oxide in alcohol (2). We found that the hydrogenation of the acyloins did not always proceed smoothly. In such cases we obtained the diols in good yield by lithium aluminum hydride reduction.

We distilled the diols through an electrically heated column of asbestos and alumina and from the mixture separated the cyclanones in poor yield as semicarbazones.

Formula Scheme
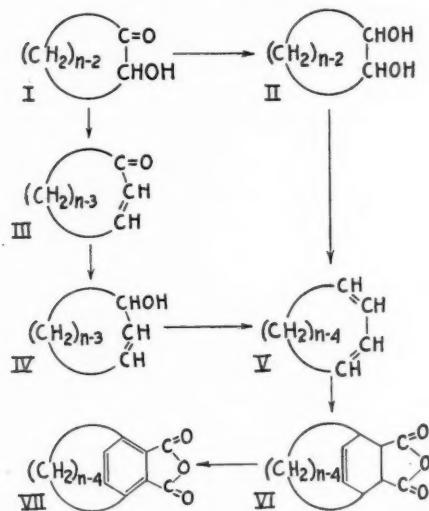
FIG. 1.

The nonketonic material was fractionated over sodium and gave good analytical results for the dienes V($n = 14$, $n = 18$). However, the yields varied, and in the average were very unsatisfactory although one of the reported experiments gave a tolerable yield.

For this reason we decided to devise another approach to the diene synthesis.

Before starting this new synthesis we made several attempts to add maleic anhydride to our dienes prepared by the dehydration of the diols. These attempts failed.

As the amount of the dienes that we had used in these experiments was limited, we do not at present, from the failure to add maleic anhydride, draw any conclusions regarding the structure of these dienes. This question will be dealt with in a later investigation.

Our second approach to the proposed synthesis, which has been more successful, is outlined in the formula scheme (I → III → IV → V → VI).

M. Stoll (4) has demonstrated that cyclic acyloins can be dehydrated in the gas phase over alumina to α-β unsaturated ketones which he, without characterization, hydrogenated to cyclanones.

After some experience we have found this dehydration very satisfactory; as a matter of fact we obtained approximately the same per cent yield whether we distilled the crude acyloin in a Hickman flask to give the pure acyloin, or over a column of heated alumina catalyst to give the α-β unsaturated ketone.

We have characterized the two unsaturated ketones III($n = 14$, $n = 18$) as semicarbazones.

The unsaturated ketones were smoothly reduced to the corresponding α-β unsaturated alcohols IV($n = 14$, $n = 18$) with lithium aluminum hydride.

The alcohols were characterized as the beautifully crystalline phenyl-urethanes, and they crystallized also to low melting solids after repeated distillation for analysis.

Finally, the alcohols were dehydrated in warm benzene by means of phosphorus pentoxide to give the dienes V($n = 14$, $n = 18$) in 70% yield. The ultraviolet spectra of these dienes showed the characteristic maxima at 232 mμ.

The Diels–Alder reaction of maleic anhydride with these dienes proved far from being smooth. At first our attempts under different conditions gave back the diene with a small amount of polymers. Finally, we obtained the desired addition products by refluxing the dienes with several moles of maleic anhydride in excess in xylene under nitrogen for five hours. But even under these conditions a great part of the hydrocarbon was recovered.

Both the addition products VI($n = 14$, $n = 18$) were isolated by saponification to the crystalline acids and reconversion to the anhydrides by high vacuum sublimation.

In a subsequent communication we shall report the results of our dehydrogenation experiments leading to VII.

Experimental Part

Cyclotetradecadiol II ($n = 14$)

Cyclotetradecanol–one–2 (5.2 gm.) was hydrogenated in 50 ml. of ethanol over 0.75 gm. of platinum oxide. The hydrogenation proceeded slowly. After two days the uptake stopped (592 ml.).

After the alcohol had been distilled off, the crude diol (5.2 gm.) was recrystallized seven times from ethyl acetate. It melted at 135°C. and was sublimed for analysis in high vacuum at 120°C. Calc. for $C_{14}H_{28}O_2$: C, 73.6; H 12.36%. Found: C 73. 68; H 12. 22%.

Dehydration of Cyclotetradecadiol

Cyclotetradecadiol (2.6 gm.) was distilled through a column (9 cm. high and 3 cm. wide) packed with a mixture of equal volumes of pure asbestos and adsorption alumina (Fisher). The temperature of the column was measured by means of an ordinary thermometer in the middle of the column and was 360°C. The pressure during the distillation was 7 mm. The distillation lasted about six hours, and 0.895 gm. of crude distillate was collected. By treatment with semicarbazide acetate a small amount of impure cyclotetradecanone semicarbazone was removed, and the nonketonic material distilled

over sodium.   Yield: 0.42 gm.   For analysis it was again fractionated over sodium in a collar flask.   It distilled at 106–108°C. (3 mm.) (outside temperature).   Calc. for $C_{14}H_{24}$: C, 87.42; H, 12.58%.   Found: C, 87.52; H, 12.51%.

Dehydration of Cyclotetradecanol–one–2 to III(n = 14)

The crude undistilled acyloin prepared according to the directions of Prelog *et al.* (2) from 20 gm. of the corresponding dicarboxylic acid dimethyl ester was distilled through the column described in the previous experiment. Column temperature was maintained at 325°C.; pressure, 4 mm.   The distillation lasted five hours.   The yield of the α-β unsaturated ketone was 7.18 gm., which is 48% based on the dicarboxylic acid ester.

A semicarbazone was prepared by treatment with semicarbazide acetate, and after four recrystallizations from methanol it melted constantly at 165–166°C.   Calc. for $C_{15}H_{27}N_3O$: N, 15.85%.   Found: N, 16.06%.

Cyclotetradecen–ol–3 IV(n = 14)

In a three necked flask equipped with a mercury seal stirrer, reflux condenser, and dropping funnel, was placed 1 liter of dry ether and 3.8 gm. lithium aluminum hydride, and the whole was refluxed for 30 min.

After this the solution was cooled and a solution of 7 gm. of the α-β unsaturated ketone in 100 ml. of ether was added over a period of two hours. The solution was then refluxed for two hours and left stirring over night at room temperature.

Sulphuric acid (280 cc., 5%) was added the next day.   The ether layer was separated and the aqueous layer extracted several times with ether.   After washing with 5% sodium carbonate and water, the ether was dried and distilled off.   In the flask remained 7.05 gm. of the oily alcohol.   It was fractionated twice in a collar flask for analysis.   After distillation it solidified to a low melting crystalline solid.   It boiled at 108–110°C. (1 mm.) (outside temperature).   Calc. for $C_{14}H_{26}O$: C, 79.90; H, 12.46%.   Found: C, 80.11, 79.92; H, 12.68, 12.50%.

The phenylurethane, recrystallized from ether–petroleum ether, melted at 105–106°C. after six crystallizations.   For analysis it was dried in high vacuum at 60°C. for 24 hr.   Calc. for $C_{21}H_{31}NO_2$: C, 76.52; H, 9.48; N, 4.25%. Found: C, 76.74, 76.87; H, 9.15, 9.34; N, 4.41, 4.35%.

Dehydration to Cyclotetradecadiene V(n = 14)

The alcohol (4.27 gm.) was dissolved in 100 ml. of absolute benzene.   The temperature was maintained at 50°C.   The solution was stirred vigorously and 20 gm. of phosphorus pentoxide added at 10 min. intervals for 40 min. After this, the mixture was cooled and decomposed with crushed ice.   The aqueous layer was extracted with ether, and the ether was combined with the benzene layer, washed with a 5% sodium carbonate solution and water, and

dried. After the solvent had been distilled off, the yield of the crude product was 3.5 gm. The product was distilled over sodium, giving 2.88 gm. of pure product, which corresponds to a yield of 74.3%. For analysis it was distilled once more in a collar flask; b.p., 97°C. at 1–2 mm. (outside temperature). Calc. for $C_{14}H_{24}$: C, 87.42; H, 12.58%. Found: C, 87.47; H, 12.62%. Density at 25° = 0.8723. $n_D^{20} = 1.4982$.

Diels–Alder Reaction of Cyclotetradecadiene and Maleic Anhydride

The diene (1 gm.), hydroquinone (10 mgm.) and maleic anhydride (2.52 gm.; 5 moles excess) were refluxed in 30 ml. of xylene in a stream of carefully purified and dried nitrogen for five hours. After this time the xylene was evaporated and the residue hydrolyzed by shaking with a solution of 5 gm. of potassium hydroxide in 25 cc. of water. The alkaline solution was extracted with ether and by working up this ether solution 0.330 gm. of diene was recovered.

The alkaline solution was then acidified, the precipitated acids extracted with ether, and the ether solution washed many times with water which removed maleic acid.

After drying, the ether solution was evaporated; 0.389 gm. of an amorphous acid remained. It crystallized readily in beautiful needles from ether–hexane and was recrystallized eight times, m.p. 139–140°C. For analysis it was dried at room temperature in high vacuum for 40 hr. Calc. for $C_{18}H_{28}O_4$: C, 70.11; H, 9.15%. Found: C, 70.33; H, 9.19%. The acid was sublimed at 120°C. (1 mm.). The sublimate was the oily anhydride. Calc. for $C_{18}H_{26}O_3$: C, 74.45; H, 9.03%. Found: C, 74.62, 74.50; H, 9.03, 8.91%.

Cycloöctadecadiol II$(n = 18)$

Cycloöctadecanol–one–2 (8.1 gm.) was dissolved in 100 ml. dry ether and added to a solution of 3.27 gm. of lithium aluminum hydride in 1000 ml. of ether. After the addition it was refluxed for two hours and then stirred overnight at room temperature. Next morning 200 ml. of 5% sulphuric acid was added and the product worked up as usual. After one recrystallization from ethyl acetate the yield of the diol was 6 gm. (74%). For analysis it was crystallized four times from ethyl acetate and sublimed at 95°C. (1 mm.). It melted at 107°C. Calc. for $C_{18}H_{36}O_2$: C, 76.00; H, 12.76%. Found: C, 75.63; H, 12.67%.

Dehydration of Cycloöctadecadiol

The experiment was conducted exactly as in the case of cyclotetradecadiol. Amount of diol, 6.0 gm.; temperature of the column, 375–400°C.; pressure, 1–3 mm. The distillation lasted eight hours. Yield of crude distillate was 3.799 gm. From the distillate 1.196 gm. of cycloöctadecanone semicarbazone was separated. The nonketonic material was distilled over sodium. Yield, 2.75 gm., which is 52.5%. This material was distilled twice more over sodium in a collar flask. It distilled at 2–3 mm. at 140°C. (outside temperature). Calc. for $C_{18}H_{32}$: C, 87.01; H, 12.99%. Found: C, 86.57; H, 13.43%.

Dehydration of Cycloöctadecanol–one–2

The experiment was conducted exactly as in the case of the C_{14} acyloin. Crude acyloin was prepared from 20 gm. of the corresponding C_{18} dicarboxylic acid dimethyl ester. Vacuum, 2–4 mm.; distillation time, nine hours; temperature of catalyst, 325°C. The yield of crude α-β unsaturated ketone was 9.4 gm., which is 57% calculated on the basis of the C_{18} dicarboxylic acid dimethyl ester. After five crystallizations from methanol the semicarbazone had a constant melting point of 183–184°C. Calc. for $C_{19}H_{35}N_3O$: C, 70.98; H, 10.98%. Found: C, 71.22; H, 11.37%.

Cycloöctadecene–ol–3 IV(n = 18)

The experiment was conducted as in the case of the corresponding C_{14} compound. The quantities used were as follows: 9.9 gm. of α-β unsaturated ketone; 4.0 gm. of lithium aluminum hydride; 1500 ml. of absolute ether. Yield: 8.342 gm. of α-β unsaturated alcohol, which is 83.7%; b.p. 122°C. (1 mm.). For analysis the product was distilled twice in a collar flask. After some time the analytical sample solidified to a very low melting crystalline solid. Calc. for $C_{18}H_{34}O$: C, 81.13; H, 12.86%. Found: C, 81.07; H, 13.03%.

The phenylurethane melted after eight crystallizations, first from ether–hexane, then from methanol, at 78–79°C. It was dried for 24 hr. at 60°C. in high vacuum. Calc. for $C_{25}H_{39}NO_2$: C, 77.87; H, 10.19; N, 3.63%. Found: C, 77.88; H, 10.21; N, 3.66%.

Dehydration to Cycloöctadecadiene V(n = 18)

The experiment was conducted as in the case of cyclotetradecadiene, using 8.342 gm. of α-β unsaturated alcohol, 31 gm. of phosphorus pentoxide, and 150 ml. absolute benzene. The diene was distilled over sodium; b.p. 115°C. (3 mm.). Yield: 5.013 gm., which is 64.5%. For analysis the diene was distilled twice more over sodium in a collar flask. Calc. for $C_{18}H_{32}$: C, 87.01; H, 12.99%. Found: C, 87.05; H, 12.95%. Density at 25°C. = 0.8814. $n_D^{20} = 1.4899$.

Diels–Alder Reaction of Cycloöctadecadiene

The experiment was conducted exactly as in the case of cyclotetradecadiene only without the addition of hydroquinone, using the following quantities: diene, 6.385 gm.; maleic anhydride, 7.202 gm.; absolute xylene, 145 ml. Recovered: 5.404 gm. of diene. The addition product was isolated by saponification to the acid and crystallization from ether–hexane. Yield: 1.410 gm.; which is 15.8% of the theoretical amount and quantitative, calculated on the basis of diene not recovered.

On crystallization from ether–hexane the acid was slowly converted to the anhydride. Since the anhydride is also crystalline in this case, it has not been possible to free the acid from the anhydride for analysis. Therefore the acid-

anhydride mixture was recrystallized six times and then converted to the anhydride by sublimation in high vacuum at 120°C. After sublimation the anhydride formed beautiful long needles, m.p. 157–158°C. Calc. for $C_{22}H_{34}O_3$: C, 76.26; H, 9.87%. Found: C,76.42; H, 9.76%.

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THE ALKALOIDS OF *LYCOPODIUM* SPECIES

XI. NATURE OF THE OXYGEN ATOM IN LYCOPODINE; SOME REACTIONS OF THE BASE[1]

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Abstract

Lycopodine gives rise to a hydrazone, is reduced to a secondary alcohol, and reacts with phenyl-lithium to form a tertiary carbinol; hence, the oxygen atom of the base is present in a keto group. The base reacts with cyanogen bromide to form two cyanobromolycopodines, α and β. α-Cyanobromolycopodine is converted by potassium acetate in alcohol to α-cyanoacetoxylycopodine, hydrolyzable to α-cyanohydroxylycopodine, which can be oxidized to an acid. The action of methanolic potassium hydroxide on α-cyanobromolycopodine gives rise to a nonoxidizable, nonreducible neutral compound, while a similar isomeric and equally inert substance is produced by the action of a boiling ethanolic solution of potassium acetate on β-cyanobromolycopodine. Both α- and β-cyanobromolycopodines are hydrogenated catalytically to two isomeric products $C_{17}H_{26}ON_2$. α-Cyanobromolycopodine with trimethylamine forms of quaternary salt which, when subjected to the conditions of the Hofmann degradation, gives rise to a base differing from the quaternary salt by the elements of methyl bromide, and to the same neutral product obtainable from α-cyanobromolycopodine by the action of methanolic potassium hydroxide.

The alkaloid lycopodine is present in all the *Lycopodium* species so far examined except in *L. cernuum* L. (7) and *L. saururus* (2a). Its empirical formula was established by Achmatowicz and Uzieblo (1) and has since been confirmed (5). The base contains no methoxyl, imino-methyl nor active hydrogen (1). It does not undergo catalytic hydrogenation under high pressures nor does it react with phenylmagnesium bromide (6), and it had been concluded that the oxygen atom was probably present in a cyclic ether linkage (6). However, it has now been shown that the oxygen atom is present in a carbonyl group. The infrared absorption spectrum of lycopodine showed an absorption band at 1693 cm.$^{-1}$ which is in the region of carbonyl absorption. This indication of the presence of a carbonyl in lycopodine has been confirmed by the formation of a hydrazone, by the reduction of the keto group to an alcohol with the aid of lithium aluminum hydride, and finally by conversion to a tertiary carbinol by the action of phenyl-lithium. Furthermore, dihydrolycopodine obtained by the action of lithium aluminum hydride had an infrared spectrum no longer showing the carbonyl band at 1693 cm.$^{-1}$, but containing a sharp band at 3625 cm.$^{-1}$, indicating the presence of a hydroxyl group.

Attempts to degrade lycopodine through its N-oxide (8), or by the Emde or the Hofmann degradations proved fruitless and in all cases gave back the original base. However, treatment of lycopodine with cyanogen bromide according to the method of von Braun (2) gave rise to two isomeric, nonbasic products, α- and β-cyanobromolycopodine ($C_{17}H_{25}ON_2Br$), undoubtedly

formed by scission of a carbon–nitrogen bond with addition of the elements of cyanogen bromide. The bromine in the α-isomer was unaffected by silver acetate in benzene or by silver oxide in acetone, but was completely removed by the action of potassium acetate in ethanol with formation of α-cyanoacetoxylycopodine and the corresponding α-cyanohydroxylycopodine. Oxidation of the latter with chromic acid in acetic acid produced an amorphous acid yielding a crystalline methyl ester $C_{18}H_{26}O_3N_2$. The oxidation, therefore, seems to have converted the alcoholic group of α-cyanohydroxylycopodine, which must be primary, into a carboxylic group. The Curtius–Schmidt degradation of the amorphous acid hydrolyzed the N–CN group, but failed to attack the carboxyl, while treatment of the silver salt of the acid with bromine according to the method of Hunsdiecker (4) merely yielded the starting material.

The action of potassium acetate on α-cyanobromolycopodine followed a different course depending on the solvent used. In ethanol the reaction was that described above, but in glacial acetic acid both the cyanogen group and the bromine were eliminated with formation of lycopodine and small quantities of two isomeric bases.

Boiling α-cyanobromolycopodine with methanolic potassium hydroxide removed the elements of hydrogen bromide and gave rise to a nonbasic compound isomeric with a substance obtained by the action of boiling ethanolic potassium acetate on β-cyanobromolycopodine. Both these isomeric products ($C_{17}H_{24}ON_2$) were resistant to oxidation with potassium permanganate, chromic acid, or ozone, and also to catalytic hydrogenation. The apparent absence of unsaturation in these isomers indicates that the removal of hydrogen bromide in their formation may have been accompanied by cyclization. Cyclization, however, did not occur when both α- and β-cyanobromolycopodine were hydrogenated catalytically: hydrogenolysis took place with the formation of reduction products ($C_{17}H_{26}ON_2$) that appear to be isomeric.

Since the Hofmann degradation of lycopodine was unsuccessful an attempt was made to degrade α-cyanobromolycopodine with the aid of a dodge. The bromo compound when treated with trimethylamine gave rise to cyanotrimethylaminolycopodine bromide. This quaternary salt was converted to the corresponding quaternary base and this was pyrolyzed *in vacuo*. It yielded two products, one of which was identical with the nonbasic substance obtained by the action of potassium hydroxide on α-cyanobromolycopodine, while the other was a base formed from the quaternary base by the loss of methanol.

Experimental

Lycopodine Hydrazone

A mixture of lycopodine (1.21 gm.), sodium hydroxide pellets (0.6 gm.), ethylene glycol (9 cc.), 85% hydrazine hydrate (0.6 cc.) and ethanol (3 cc.) was refluxed for one hour in an oil bath. The reflux condenser was removed

and heating continued until the temperature of the reaction mixture had reached 196°C. The condenser was then replaced and the heating continued a further three hours. After cooling, the reaction mixture was diluted with water and extracted repeatedly with ether. The combined extract was dried over sodium chloride and distilled to dryness on the steam bath. There was left a residue consisting of a light brown oil which crystallized on standing, wt. 1.22 gm. After four recrystallizations from a mixture of methanol and absolute ether, the substance consisted of stout, colorless prisms, m.p. 208–210°.* This substance was not the expected reduced base, but the hydrazone of lycopodine. Calc. for $C_{16}H_{27}N_3$: C, 73.57; H, 10.11; N, 16.09%. Found: C, 73.36, 73.31; H, 9.85, 9.95; N, 16.26, 16.12%.

Some of the hydrazone was dissolved in methanol and converted to perchlorate by making the solution just acid to Congo red with 65% perchloric acid. The perchlorate crystallized immediately; it was filtered and recrystallized twice from boiling methanol from which it separated as colorless prismatic needles, m.p. 257°C. (dec.). Calc. for $C_{16}H_{27}N_3.HClO_4$: C, 53.11; H, 7.75; N, 11.61%. Found: C, 52.99, 53.03; H, 7.65, 7.78; N, 10.24, 10.42%.

An attempt was made to prepare lycopodine semicarbazone by substituting semicarbazide for the hydrazine hydrate in the above reaction, but unchanged lycopodine was recovered.

Dihydrolycopodine

Into a dry flask, equipped with a reflux condenser and a side arm carrying a gas inlet tube and previously swept with dry nitrogen, were introduced first a solution of lycopodine (1.0 gm.) in absolute ether (15 cc.) and then absolute ether (15 cc.) containing 2 cc. of a 12% ethereal solution of lithium aluminum hydride. This last addition was made dropwise and at such a rate as to maintain a slight reflux. After the addition of the hydride, the refluxing was maintained for 30 min. After the reaction mixture had cooled, aqueous methanol was added while the flask was kept cooled in ice water. The precipitated aluminum hydroxide was filtered and the filtrate extracted repeatedly with chloroform. The combined extract was evaporated and the crystalline residue (wt. 0.95 gm.) recrystallized from ether, from which it separated as beautiful colorless prisms, m.p. 168°C. Calc. for $C_{16}H_{27}ON$: C, 77.10; H, 10.84; N, 5.63%. Found: C, 77.05, 76.90; H, 10.59, 10.40; N, 5.52, 5.69%.

The mother liquor from the recrystallization of dihydrolycopodine was evaporated to dryness, the residue dissolved in methanol, and the solution made just acid to Congo red by the dropwise addition of 65% perchloric acid. Dilution of the resulting solution with ether caused the separation of a crystalline perchlorate which, after several recrystallizations from methanol–ether, consisted of very small colorless prisms, m.p. 223-224°C. Calc. for $C_{16}H_{27}ON.HClO_4$: C, 54.90; H, 8.01; N, 4.00%. Found: C, 55.02, 54.91; H, 7.81, 7.92; N, 4.11, 4.06%.

All melting points are corrected.

Reaction of Lycopodine with Phenyl-lithium

Lycopodine (1.8 gm.) was dissolved in dry ether and the solution added dropwise with stirring to an ether solution of phenyl-lithium prepared from lithium (0.30 gm.) and bromobenzene (3.10 gm.) (3). An exothermic reaction resulted and, after complete addition of the base, the mixture was refluxed for one hour. The reaction mixture was poured into acetic acid and ice and the resulting solution extracted with ether. The aqueous solution was alkalized with sodium hydroxide and extracted repeatedly with ether. This second ether extract was evaporated to a small volume from which a base crystallized (0.7 gm.), m.p. 154-155°C. Calc. for $C_{22}H_{31}ON$: C, 81.23; H, 9.54; N, 4.30%. Found: C, 81.22, 81.44; H, 9.73, 9.91; N, 4.22%.

The ether mother liquor from which the base had crystallized was evaporated to dryness, the residue dissolved in ethanol, and the solution neutralized with perchloric acid. A crystalline perchlorate (1.0 gm.) was obtained which proved identical with that prepared as follows. A small quantity of the crystalline base was dissolved in ethanol and the solution made just acid to Congo red by the cautious addition of 65% perchloric acid. The perchlorate that separated contained ethanol of crystallization; it sintered at 140° C. and melted indefinitely, becoming completely liquid at 208°C. Calc. for $C_{22}H_{31}ON$. $HClO_4 . C_2H_6O$: C, 61.08; H, 8.06; N, 2.97%. Found: C, 60.89, 61.04; H, 8.09, 8.22; N, 2.97%.

Reaction of Lycopodine with Cyanogen Bromide

To a solution of lycopodine (1.5 gm.) in chloroform, cyanogen bromide (3 gm.) was added and the mixture kept in the refrigerator for 16 hr., after which the solvent was distilled off on the steam bath. The residue was triturated with ether, in which it was only partially soluble. The insoluble fraction was dissolved in boiling ethanol from which it crystallized on cooling. After recrystallization from ethanol it melted at 360°C. and proved to be identical with lycopodine hydrobromide. Yield, 5–10%. Calc. for $C_{16}H_{25}ON.HBr$: C, 58.53; H, 7.92; N, 4.29%. Found: C, 58.62, 58.57; H, 8.17, 8.22; N, 4.27%.

The ether solution containing the soluble fraction of the reaction product was washed with dilute hydrochloric acid, dilute sodium hydroxide, and water. After drying over anhydrous sodium sulphate the solvent was distilled off and the residue redissolved in ether. The solution was filtered to remove a small quantity of insoluble material, concentrated to a small volume, and chilled in the refrigerator when the product crystallized. After recrystallization from ether it melted at 140°C.; yield 50–60%. This compound will be designated α-cyanobromolycopodine. Calc. for $C_{17}H_{25}ON_2Br$: C, 57.79; H, 7.08; N, 7.93%. Found: C, 57.40, 58.07; H, 7.34, 7.36; N, 8.24%.

The mother liquor from the crystallization of α-cyanobromolycopodine was concentrated and allowed to stand in the refrigerator. A second product

crystallized which, after recrystallization from ether, melted at 108–109°C. This product was isomeric with the first and will be designated β-cyanobromolycopodine. Calc. for $C_{17}H_{25}ON_2Br$: C, 57.79; H, 7.08; N, 7.93%. Found: C, 57.82, 57.90; H, 6.68, 6.63; N, 7.72%.

α–Cyanoacetoxylycopodine

α-Cyanobromolycopodine (0.7 gm.) was refluxed for 12 hr. with potassium acetate (2 gm.) in ethanol (50 cc.). The ethanol was evaporated on the steam bath and water added to the residue. The resulting mixture was extracted with ether and the extract dried over sodium sulphate and distilled to remove the solvent. An oily residue was left which partially crystallized when dissolved in ether and the resulting solution cooled, wt. 0.1 gm. After recrystallization from ether it melted at 112–113°C. Calc. for $C_{19}H_{28}O_3N_2$: C, 68.67; H, 8.43; N, 8.43%. Found: C, 68.58, 68.90; H, 8.53, 8.40; N, 8.17, 8.40%.

The oily residue recovered from the ether mother liquor of the crystallization of α-cyanoacetoxylycopodine was dissolved in chloroform and chromatographed on alumina. The adsorbed material was eluted first with chloroform and then with chloroform–methanol. One of the fractions thus obtained yielded a further small quantity of α-cyanoacetoxylycopodine, while the main fraction in benzene solution was chromatographed again on alumina and eluted with benzene and then with benzene–methanol. It yielded an oily hydroxylic substance which by the action of boiling acetyl chloride containing a trace of pyridine was converted into α-cyanoacetoxylycopodine, m.p. 112–113°C.

Reaction of β-Cyanobromolycopodine with Potassium Acetate in Ethanol

A quantity of β-cyanobromolycopodine was refluxed for six hours with a large excess of potassium acetate in ethanol. The ethanol was distilled off, water added to the residue, and the mixture extracted with ether. Distillation of the extract on the steam bath to remove the ether left a halogen-free oily residue. This residue was refluxed with potassium hydroxide in ethanol to hydrolyze any acetyl group, the ethanol distilled off, water added to the residue, and the mixture extracted with ether. Evaporation of the ether extract left an oily residue which was dissolved in benzene and chromatographed on alumina. Elution with benzene yielded two fractions while elution with benzene–methanol yielded a third. The second fraction was crystalline and after recrystallization from ether–hexane melted at 102°C. Calc. for $C_{17}H_{24}ON_2$: C, 75.00; H, 8.82; N, 10.29%. Found: C, 75.60, 75.00; H, 9.12, 9.17; N, 10.07, 10.03%. The first fraction consisted of a trace of oil soluble in ether but insoluble in methanol, while fraction III could not be induced to crystallize. The crystalline product was inert to oxidation and to hydrogenation.

Hydrolysis of α-Cyanoacetoxylycopodine

α-Cyanoacetoxylycopodine (1.0 gm.) was refluxed for two hours with potassium hydroxide (1.0 gm.) in methanol (20 cc.) and then heated on the

steam bath under reduced pressure to remove the solvent. Water was added to the residue and the mixture extracted with ether. Removal of the ether by distillation of the extract on the steam bath left an oily residue that partially crystallized on long standing. After recrystallization from ether–hexane, α-cyanohydroxylycopodine melted at 97°C. Calc. for $C_{17}H_{26}O_2N_2$: C, 70.34; H, 8.97; N, 9.65%. Found: C, 70.74, 70.92; H, 9.58, 9.59; N, 8.95, 9.05%.

The fraction of the product that had not crystallized (1.0 gm.) was dissolved in glacial acetic acid containing a few drops of sulphuric acid and to this solution, after warming to 50–60°C., a concentrated aqueous solution of chromic acid was added dropwise until the yellow color was persistent. The excess chromic acid was reduced by the addition of a little methanol, and the acetic acid was distilled under reduced pressure. Water was added to the residue and the mixture extracted with chloroform. The extract when evaporated to dryness yielded a crude acid (0.6 gm.) which failed to crystallize. The acid was dissolved in methanol and added to an ethereal solution of diazomethane. After the resulting solution had been left standing for some time the excess diazomethane and the solvent were removed by distillation and the residual methyl ester distilled *in vacuo*. It boiled at 205–210°C. (0.05 mm.), yield 75% based on the weight of crude acid; it crystallized on standing and, after recrystallization from ether, melted at 82–83°C. Calc. for $C_{18}H_{26}O_3N_2$: C, 67.92; H, 8.14; N, 8.80%. Found: C, 67.94, 68.16; H, 8.69, 8.52; N, 8.66, 8.64%. The Curtius degradation of the acid did not follow a normal course. An attempt to replace the carboxylic group with bromine by treating the silver salt of the acid with bromine according to Hunsdiecker (4) yielded the unchanged acid.

Reduction of α-Cyanobromolycopodine

α-Cyanobromolycopodine (0.2 gm.), dissolved in methanol (25 cc.) containing potassium hydroxide (1 gm.) was hydrogenated under a pressure of 40 lb. for six hours in the presence of 2% palladium – calcium carbonate catalyst (0.2 gm.). The catalyst was filtered and the filtrate distilled on the steam bath to remove the methanol. Water was added to the residue and the mixture extracted repeatedly with ether. The combined ether extract was concentrated to a small volume and allowed to stand in a stoppered flask. A crystalline product separated which, after recrystallization from ether–hexane, melted at 130–131°C. Calc. for $C_{17}H_{26}ON_2$: C, 74.45; H, 9.48; N, 10.25%. Found: C, 74.42, 74.12; H, 9.18, 9.14; N, 10.14%.

Reduction of β-Cyanobromolycopodine

β-Cyanobromolycopodine was reduced under exactly the same conditions described for the α-isomer. It yielded a product which after distillation *in vacuo* consisted of a resin that crystallized after several weeks. Even after recrystallization from ether–hexane, it melted over a range, 73–90°C. The resin, before crystallization, yielded the following analytical figures: C, 75.21,

75.27; H, 9.04, 9.21; N, 10.14%. The crystalline product: C, 74.94, 75.25; H, 8.84, 9.02; N, 9.96, 9.99%. Calc. for $C_{17}H_{26}ON_2$: C, 74.45; H, 9.48; N, 10.25%.

Action of Potassium Hydroxide on α-Cyanobromolycopodine

α-Cyanobromolycopodine (0.9 gm.) was refluxed for six hours with potassium hydroxide (2 gm.) in methanol (30 cc.). The solvent was distilled under reduced pressure on the steam bath and the residue diluted with water which caused the separation of a brown crystalline solid. The mixture was extracted with ether which dissolved the crystals and the extract washed with dilute hydrochloric acid, with water and dried over sodium sulphate. The ether solution was filtered and concentrated to a small volume from which a crystalline solid separated, m.p. 143–144°C. In admixture with the starting material it melted at 95–105°C. It gave a negative Beilstein halogen test, was resistant to oxidation by ozone, potassium permanganate or chromic acid, and resistant to hydrogenation in methanolic solution over Adams' catalyst at a pressure of 22 lb. Calc. for $C_{17}H_{24}ON_2$: C, 75.00; H, 8.82; N, 10.29%. Found: C, 74.83, 75.13; H, 9.02, 9.29; N, 10.13%. This product is isomeric with that obtained by the action of potassium acetate in ethanol on β-cyanobromolycopodine, which is similarly inert.

α-Cyanotrimethylaminolycopodine Bromide

To a solution of α-cyanobromolycopodine (0.48 gm.) in methanol an excess of trimethylamine was added and the solution kept in the refrigerator for 24 hr. The solvent and excess amine were removed by evaporation on the steam bath and the residue was dissolved in acetone. A white solid immediately crystallized which after recrystallization from methanol–acetone melted at 259–260°C. Calc. for $C_{20}H_{34}ON_3Br$: C, 58.25; H, 8.25; N, 10.25%. Found: C, 58.17, 58.35; H, 8.09, 8.10; N, 9.75, 10.07%.

An aqueous solution of the quaternary bromide thus obtained was shaken with freshly precipitated silver oxide, filtered, and evaporated to dryness on the steam bath. The residue was then heated *in vacuo*. Decomposition started at 120–130°C. (0.5 mm.) and when this had subsided the temperature was raised. A distillate (0.37 gm.) was collected at 180–200°C. (0.5 mm.). The distillate was dissolved in ether and the solution extracted with dilute hydrochloric acid. The ether solution was concentrated on the steam bath and allowed to stand. A crystalline substance separated which melted at 143–144°C. either alone or after admixture with the product of the action of potassium hydroxide on α-cyanobromolycopodine ($C_{17}H_{24}ON_2$). The acid extract from the ether solution was alkalinized with ammonia and extracted with ether. The ether solution was evaporated to dryness, the residue dissolved in acetone, and the solution made just acid to Congo red by the cautious addition of 65% perchloric acid. A perchlorate crystallized which was recrystallized from boiling acetone; it melted at 230–231°C. (dec.). Calc. for $C_{19}H_{31}ON_3 \cdot HClO_4$: C, 54.82; H, 7.67; N, 10.06%. Found: C, 54.58, 55.04; H, 7.85, 7.99; N, 10.06%.

Acknowledgment

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PRELIMINARY TESTS ON POSSIBLE NEW STABILIZERS FOR NITROCELLULOSES[1]

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AND C. B. PURVES

Abstract

It was assumed that any practical stabilizer for nitrocellulose would have to meet the following requirements: (a) absorb nitrogen dioxide at least as avidly as the accepted stabilizer, sym-diethyldiphenylurea (Centralite); (b) cause destruction of nitrocellulose in the Bergmann–Junk heat test no greater than that caused by the accepted stabilizer, diphenylamine; (c) be no less compatible than diphenylamine with nitrocellulose; and (d) melt no higher than 80°C., have low volatility and low solubility in water. These requirements were met by N,N'-diethyl-N,N'-di-(3-methoxy-4-ethoxybenzyl)-urea, N,N'-diethyl-N,N'-di-(3,4-dimethoxybenzyl)-succinamide, di-(3,4-dimethoxystyryl)-ketone, and perhaps by veratric aldehyde. The criteria, however, were quite inadequate to assess in a positive way any practical value of the above substances as stabilizers. A study of substances structurally related to those already mentioned revealed no correlation between avidity for nitrogen dioxide and efficiency in improving the results of the Bergmann–Junk test.

Sym-N,N'-diethyl-N,N'-di-(3,4-dimethoxybenzyl)-succinamide and N-ethyl-N-propionyl-3,4-dimethoxybenzylamine were oils thought to be new, and sym-N,N'-diethyl-N,N'-dibenzylurea was obtained by an alternate procedure.

Introduction

Standard accounts (41, pp. 640-645) note that nitrocelluloses, even when carefully prepared, during storage liberate oxygenated nitrogen compounds, one or more of which act as catalysts for further decomposition. The onset of the dangerous autocatalytic second phase of the decomposition is greatly delayed when the nitrocellulose is intimately blended with a small percentage of chalk, sodium silicate, or carbonate (1, 28, 29, 43), ammonia (46), petroleum jelly (36, 53-56), and glycerides (44) containing unsaturates, phenanthrene (56), tartaric and other polybasic acids (24), amyl alcohol (4, 31), dimethylaniline (59), dicyandiamide (45), carbazole (9, 14), diphenylbenzidine (31) or triphenylamine (47). This list, although highly incomplete, illustrates the wide variety of chemical types that have been claimed as stabilizers for nitrocelluloses. Consideration has shown that the property common to such types is a capacity to combine with, and so to destroy, nitrogen dioxide, nitrous and nitric acids, either by virtue of a slightly basic character, or by some kind of chemical unsaturation or substitution (4). Substances of pronounced basicity, however, are useless as stabilizers because they decompose the nitrocellulose on their own account (2). Other properties desirable in stabilizers include

compatibility with nitrocellulose (31); low volatility and low solubility in water, lest they be lost from the explosive during long storage in humid conditions; and a melting point well below 100°C., so that they can be incorporated readily with the nitrocellulose in the form of an emulsion in hot water. Diphenylamine has been used on a large scale as a stabilizer since about 1910 (6, 16, 49) but now has to compete with Centralite (*sym*-diethyldiphenylurea), which is more compatible with nitrocellulose (16), and has other advantages (37, 38, 39). Other mono- and di-alkylated phenylureas (Akardites) have also been considered as stabilizers (55, 56). The present article originated in attempts to assess the suitability, as stabilizers for nitrocellulose, of several new compounds chemically related to Centralite but derived from methylated and ethylated vanillin (18, 19, 20). It seemed probable that vanillin could readily be produced on a large scale from the waste liquors of the wood pulping industry, and that the presence of alkoxyl groups in stabilizers might influence their chemical and physical properties in favorable ways. The complete list of substances studied (Table I) includes some previously described by other workers and some not derived from vanillin. With the exception of the vanillins, Centralites and diphenylamine, preparations for substances with no reference number in the table are given in the Experimental portion.

TABLE I

STRUCTURES OF SUBSTANCES EXAMINED

I. *Diphenyl ureas*
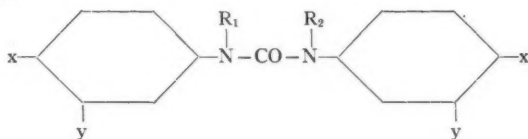
Ia. N,N'-Diethyl-N,N'-diphenylurea (Centralite)
$R_1 = R_2 = C_2H_5$; $x = y = H$. $C_{17}H_{20}ON_2$. Mol. wt. 268.

Ib. N,N'-Dimethyl-N,N'-diphenylurea (Methylcentralite)
$R_1 = R_2 = CH_3$; $x = y = H$. $C_{15}H_{16}ON_2$. Mol. wt. 240.

Ic. N,N'-Diethyl-N,N'-di-(3,4-dimethoxyphenyl)-urea. (Ref. 19.)
$R_1 = R_2 = C_2H_5$; $x = y = OCH_3$. $C_{21}H_{28}O_5N_2$. Mol. wt. 388.

Id. N,N'-Diethyl-N,N'-di-(3-methoxy-4-ethoxyphenyl)-urea. (Ref. 19.)
$R_1 = R_2 = C_2H_5$; $x = OC_2H_5$; $y = OCH_3$. $C_{23}H_{32}O_5N_2$. Mol. wt. 416.

Ie. N-Ethyl-N,N'-di-(3-methoxy-4-ethoxyphenyl)-urea. (Ref. 19.)
$R_1 = C_2H_5$; $R_2 = H$; $x = OC_2H_5$; $y = OCH_3$. $C_{21}H_{28}O_5N_2$. Mol. wt. 388.

If. N,N'-Di-(3-methoxy-4-ethoxyphenyl)-urea. (Ref. 19.)
$R_1 = R_2 = H$; $x = OC_2H_5$; $y = OCH_3$. $C_{19}H_{24}O_5N_2$. Mol. wt. 360.

II. *Dibenzylureas*
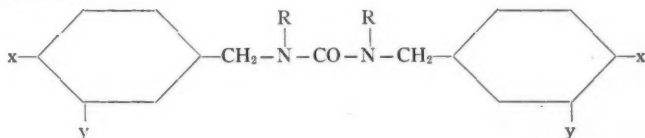
II*a*. N,N′-Diethyl-N,N′-di-(3,4-dimethoxybenzyl)-urea. (Ref. 18.)
  R = C_2H_5; x = y = OCH_3. $C_{23}H_{32}O_5N_2$. Mol. wt. 416.

II*b*. N,N′-Diethyl-N,N′-di-(3-methoxy-4-ethoxybenzyl)-urea. (Ref. 18.)
  R = C_2H_5; x = OC_2H_5; y = OCH_3. $C_{25}H_{36}O_5N_2$. Mol. wt. 444.

II*c*. N,N′-Di-(3-methoxy-4-ethoxybenzyl)-urea. (Ref. 18.)
  R = H; x = OC_2H_5; y = OCH_3. $C_{21}H_{28}O_5N_2$. Mol. wt. 388.

II*d*. N,N′-Diethyl-N,N′-dibenzylurea.
  R = C_2H_5; x = y = H. $C_{19}H_{24}ON_2$. Mol. wt. 296.

III. *Dibenzyl diamides*
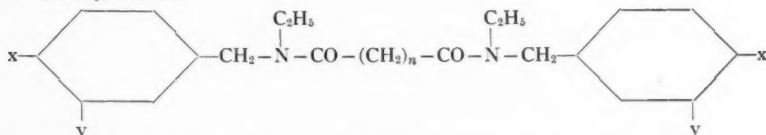
III*a*. N,N′-Diethyl-N,N′-di-(3-methoxy-4-ethoxybenzyl)-oxamide. (Ref. 20.)
  x = OC_2H_5; y = OCH_3; n = 0. $C_{26}H_{36}O_6N_2$. Mol. wt. 472.

III*b*. N,N′-Diethyl-N,N′-di-(3,4-dimethoxybenzyl)-succinamide.
  x = y = OCH_3; n = 2. $C_{26}H_{36}O_6N_2$. Mol. wt. 472.

III*c*. N,N′-Diethyl-N,N′-di-(3-methoxy-4-ethoxybenzyl)-succinamide. (Ref. 20.)
  x = OC_2H_5; y = OCH_3; n = 2. $C_{28}H_{40}O_6N_2$. Mol. wt. 500.

III*d*. N,N′-Diethyl-N,N′-dibenzyl succinamide. (Ref. 20.)
  x = y = H; n = 2. $C_{22}H_{28}O_2N_2$. Mol. wt. 352.

IV. *Distyryl ketones*
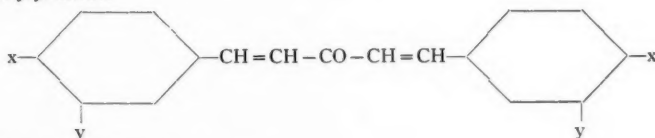
IV*a*. Di-(3,4-dimethoxystyryl)-ketone.
  x = y = OCH_3. $C_{21}H_{22}O_5$. Mol. wt. 354.

IV*b*. Di-(3-methoxy-4-ethoxystyryl)-ketone
  x = OC_2H_5; y = OCH_3. $C_{23}H_{26}O_5$. Mol. wt. 382.

IV*c*. Distyryl ketone.
  x = y = H. $C_{17}H_{14}O$. Mol. wt. 234.

IV*d*. Di-(3,4-methylenedioxystyryl)-ketone.
  xy = O–CH_2–O. $C_{19}H_{14}O_5$. Mol. wt. 322.

V. *Vanillins*

V*a*. Veratric aldehyde. $C_9H_{10}O_3$. Mol. wt. 166.
V*b*. Ethylated vanillin. $C_{10}H_{12}O_3$. Mol. wt. 180.
V*c*. Vanillin. $C_8H_8O_3$. Mol. wt. 152.

Miscellaneous

VI. Diphenylamine. $C_{12}H_{11}N$. Mol. wt. 169.
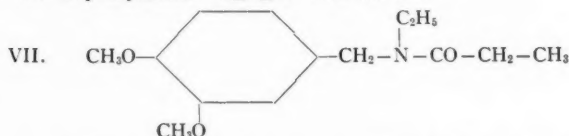
  N-Ethyl-N-propionyl-3,4-dimethoxybenzylamine. $C_{13}H_{19}O_3N$. Mol. wt. 237.

VIII. Difurfurylidene acetone. $C_{13}H_{10}O_3$. Mol. wt. 214.

IX. 3-Methoxy-4-ethoxycinnamic acid amide. $C_{12}H_{15}O_3N$. Mol. wt. 221. (Ref. 20.)

Hale (22) and also Vieille (58) considered that nitric oxide, as well as nitrogen dioxide, decomposed cellulose nitrate catalytically, but the unsaturates in petroleum jelly, an efficient stabilizer, had no effect on nitric oxide (36). The catalytic action of the latter gas was therefore unlikely, since failure of a known stabilizer to remove it failed to cause instability.

Results and Discussion

In order to confirm the irrelevance of any production of nitric oxide in the decompositions, 0.5 gm. samples of powdered diphenylamine and Centralite were distributed in glass wool and confined in a fixed volume of the pure gas at room temperature and atmospheric pressure. Careful experiments recorded no decrease in pressure caused by the absorption of the gas, and negative results were likewise obtained with pure nitrous oxide. Pure nitrogen dioxide, however, was so avidly absorbed that it had to be diluted with pure nitrogen to a partial vapor pressure of 42 mm. of mercury before rate measurements could be made. In these circumstances diphenylamine, Centralite, and all the other substances in Table I except veratric aldehyde (Va) adsorbed nitrogen dioxide very rapidly for not more than one minute. All then displayed a very much slower secondary absorption. The vanillin group (V) showed much less absorptive capacity than the others. Since the maximum absorption observed after one minute was only 0.038 mole per mole of sample, and only 0.048 mole after five minutes (with sample IIc), it was clear that the reactions were of a surface nature and probably did not reflect intrinsic ability to absorb nitrogen dioxide. Details of these experiments have therefore been omitted from this article.

A more satisfactory form of the nitrogen dioxide absorption test was to carry it out, as Frankland and Farmer (17) recommended, in carbon tetrachloride solution. Fifty cubic centimeters of each solution contained 2.09 millimoles of nitrogen dioxide and 0.375 millimoles of the sample. Aliquots were permitted to displace acetic acid from a sodium acetate solution and the decrease in the resulting acidity as time went on was taken as a measure of the nitrogen dioxide consumed. This method obviously counted any acidic products formed in the reaction as unchanged nitrogen dioxide. Figs. 1 to 4 reproduce the initial portions of the rate of absorption plots, but many of the observations made during the first 100 min. are omitted to avoid confusion. With the exception of plot (Ie), the initial rapid absorption was followed by a slow consumption that was still proceeding after 1000 min., when the observations were terminated. Extrapolation of the later, nearly linear portions of the plots to zero time gave the approximate nitrogen dioxide uptake during the initial rapid absorption, and these values, together with those at 1000 min., are listed in Table II.

TABLE II

DATA ON FACTORS RELEVANT TO STABILIZING POWER

Compound	M.p., °C.	Moles NO_2 in CCl_4*		B.J.M. tests† Mgm. NO × 10^2
		Fast	1000 min.	
Centralites				
Ia	72	0.9	1.75	90, 115, 102
Ib	123	0.8	1.5	(34) 82
Ic	79	~1.8	3.6	289, 336‡
Id	50.5	~2.1	2.6	354, 353‡
Ie	126	2.0	2.0	263, 296
If	208	1.6	—	—
Dibenzylureas				
IIa	85	0.027§	0.033§	172, 172
IIb	72	2.1	2.7	103, 130
IIc	185	0.038§	0.048§	—
IId	56.5	—	—	26
Dibenzyl diamides				
IIIa	85-86	1.8	2.7	164, 168
IIIb	Oil	—	—	81, 81
IIIc	125	2.0	3.0	100, 110
IIId	75	0.6	1.1	121, 169
Distyryl ketones				
IVa	78-80	2.4	3.25	86, 96
IVb	121-123	2.5	(3.2)	100, 100
IVc	112	1.0	1.6	78, 69
IVd	188	—	—	114, 122
Vanillins				
Va	43	0.5	1.4	112, 120
Vb	65	0.25	1.2	140, 150
Vc	81	0.033§	0.04§	97, 100
Miscellaneous				
VI	53	2.0	3.5	92, 126, 144
VII	Oil	1.4	2.1	132, 134
VIII	58-60	3.1	3.45	Expl. 104
IX	186	—	—	61, 67

*Adsorption from carbon tetrachloride solution at room temperature.

†Nitrocellulose films with 2% stabilizer cast from acetone solution and heated for 48 hr. at 55°C. B.J.M. values on nitrocellulose control 84, 86 = 85 × 10⁻² mgm. nitric oxide per gram sample.

‡B.J.M. on nitrocellulose control 99 × 10⁻² mgm. nitric oxide per gram sample. Tests by L. D. Hayward.

§Adsorption of gaseous nitrogen dioxide at 42 mm. pressure and room temperature initially and after five minutes.

Fig. 1 reveals that neither Ethylcentralite (I*a*) nor Methylcentralite (I*b*) was outstanding in its capacity to absorb nitrogen dioxide from carbon tetrachloride solution. Although the compounds formed were not investigated, they were undoubtedly similar to the mononitrocentralite, phenylethylnitrosamine, and *p*-nitrophenylethylnitrosamine isolated by Lécorché and Jovinet (26, 27) from an aged nitrocellulose–nitroglycerine explosive originally stabilized with Centralite. Methods for estimating such compounds are now available (42). Since the absorption depended in part on the nitration of the aromatic nuclei in the stabilizer and since the presence of alkoxyl groups in these nuclei would facilitate the nitration process, the increased rate and degree
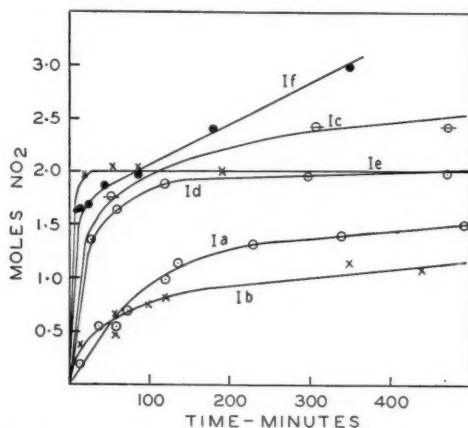
FIG. 1. *Consumption of 0.042 M nitrogen dioxide in carbon tetrachloride at room temperature. Ordinates: moles nitrogen dioxide per mole sample. For compounds Ia to If see Table I.*
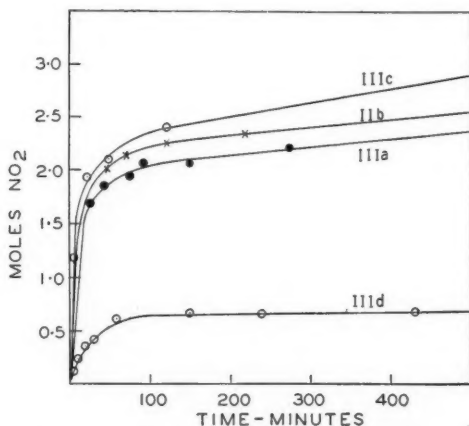
FIG. 2. *Consumption of 0.042 M nitrogen dioxide in carbon tetrachloride at room temperature. Ordinates: moles nitrogen dioxide per mole sample. For compounds IIb to IIId see Table I.*
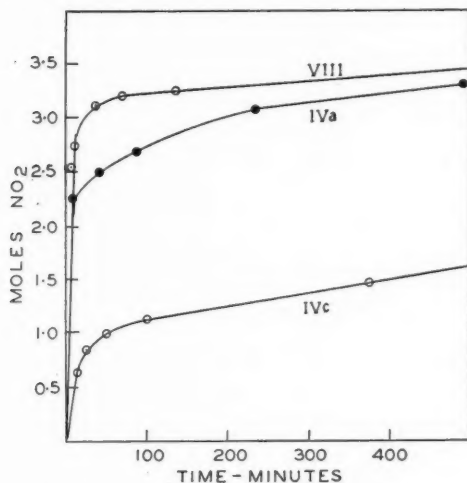
Fig. 3.   *Consumption of 0.042 M nitrogen dioxide in carbon tetrachloride at room temperature.*
Ordinates: moles nitrogen dioxide per mole sample.   For compounds IV and VIII see Table I.
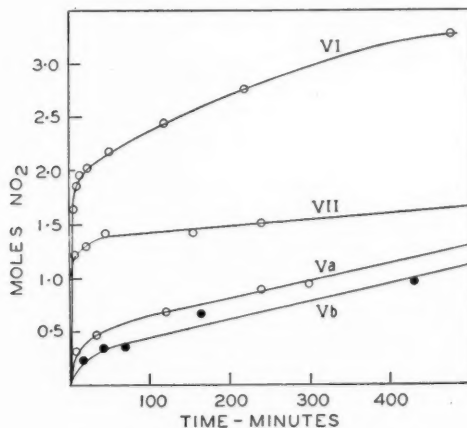
Fig. 4.   *Consumption of 0.042 M nitrogen dioxide in carbon tetrachloride at room temperature.*
Ordinates: moles nitrogen dioxide per mole sample.   For compounds V to VII see Table I.

of reaction displayed by the alkoxyl derivatives of Centralite (Ic and Id) was
not unexpected.   Replacement of the $-NC_2H_5-CO-NC_2H_5-$ unit in (Id) by
the $-NH-CO-NH-$ grouping in (If) increased the secondary absorption
markedly, but for unknown reasons replacement by $-NH-CO-NC_2H_5-$
abolished the secondary effect and caused an almost instantaneous absorption
of 2.0 moles of nitrogen dioxide (Ie).

Comparison of (I*d*) with (II*b*) (Fig. 2) showed that the change from an aniline to a benzylamine derivative also definitely increased the extent of the absorption. This increase was at first attributed to the fact that the nitrogen atom in benzylamine was much more basic in character than that in aniline. To offset this factor, the ratio of acidic carbonyl groups to nitrogen atoms was increased from 1:2 in the ureas (I*d*) and (II*b*) (−NEt−CO−NEt−) to 2:2 (−NEt−CO−CO−NEt−) in the oxamide (III*a*) and succinamide (III*c*) (−NEt−CO−CH₂CH₂CO−NEt−). Since the rate plots (II*b*), (III*a*) and (III*c*) remained close together, the variation in the nitrogen–carbonyl relationship played only a minor part in the reaction with nitrogen dioxide. In both (III*c*) and (III*d*), the amine groups were remote from the aromatic rings and presumably failed to activate the latter toward nitrating agents. This assumption suggested that the low level of absorption characteristic of (III*d*) could be attributed primarily to the −NEt−COCH₂−CH₂−CO−NEt− group, and that the marked increase in passing to (III*c*) represented nitration in aromatic rings activated, not by the amino group as in Centralite, for example, but by alkoxyl groups.

If such were the case, good absorption of nitrogen dioxide might be possessed by nonnitrogenous aromatic substances activated by alkoxyl groups and containing unsaturated side chains. This consideration, together with the desirability of retaining a carbonyl group to promote compatibility with nitrocellulose, led to the examination of the unsaturated ketones listed in Table I. The absorption of nitrogen dioxide by distyryl ketone (Fig. 3, plot IV*c*), credited in the main to the unsaturated side chain −CH=CH−CO−CH=CH−, was greatly increased by substituting the distyryl ketone with alkoxyl groups (IV*a*). Similar high absorptions were attained by difurfurylidene acetone (VIII), in which reactive furfural rings replaced the activated aromatic units in (IV*a*).

When it is remembered that the method of estimation counted acidic byproducts like nitric acid as unchanged nitrogen dioxide, the almost instantaneous apparent absorption of two moles by diphenylamine (Fig. 4, (VI)) showed that the initial reaction at once proceeded beyond the diphenylnitrosamine stage,

$$(C_6H_5)_2NH + 2\ NO_2 \longrightarrow (C_6H_5)_2N-NO + HNO_3$$

which required an apparent consumption of only one mole. Davis and Ashdown (10, 11) noted that diphenylnitrosamine in the presence of nitrous or nitric acids readily rearranged to *p*-nitrosodiphenylamine, which readily yielded di- and trinitro derivatives. Some of these derivatives were recovered from an aged smokeless powder originally stabilized with diphenylamine (3, 11). This case illustrates once more the activating influence of the amino group on aromatic nitration with nitrogen dioxide. Disregarding the change from the 3,4-dimethoxy to the 3-methoxy-4-ethoxy series, the benzyl-N-ethyl-propionamide (VII) corresponded in its structure to either half of the symmetrical dibenzylsuccinamide (III*c*); in consequence its absorption at all times was

approximately half that shown by (IIIc), and was attributed in the main to the activating action of the alkoxyl groups.   Methylated and ethylated vanillin (Va and Vb) retained the activated aromatic nucleus and the carbonyl group characteristic of most of the substances studied.   Although their uptake of nitrogen dioxide was low on a molar basis, each contained only one aromatic unit, and on a weight basis each happened to be about as effective as Ethyl-centralite (Fig. 2, Ia).   Since the latter was a proven stabilizer but nevertheless was not exceptional in its affinity for nitrogen dioxide (Fig. 1), the above absorption tests failed to eliminate any of the compounds in Table I from consideration as potential stabilizers.

The next test involved casting films from an acetone solution of a uniform, technical nitrocellulose (N, 12.6%) containing 2% of the proposed stabilizer. A thorough examination of these films for stability (3, 55) would undoubtedly require prolonged storage under ordinary conditions and the estimation, from time to time, of the amount of original stabilizer that remained intact (15, 40, 60).   Since such an examination demanded much more time and much greater amounts of material than were available, consideration was given to rapid small-scale stability tests, whose relative merits have been repeatedly discussed (5, 35, 50, 51, 52).   Control films containing diphenylamine or Centralite were first submitted to a vacuum stability test, in which the volume of gases evolved from samples heated at 100°C. or 125°C. *in vacuo* was plotted against time.   Small amounts of liquid acetone were evolved and the shape and position of the plots depended greatly on the time and temperature used in the preliminary drying of the films.   In general, films containing Centralite evolved gases at a higher rate than control films of nitrocellulose alone, but the use of diphenylamine gave irreproducible and highly variable results.   A few tests at 135°C. with methyl violet paper showed that films containing diphenylamine were the first to give the color change indicating incipient decomposition, followed by those with Centralite and finally the nitrocellulose controls.

All of the systematic work was finally carried out with the Bergmann–Junk–Mayrhofer test (30, 33, 34), in which 2 gm. samples of the films were heated at 135°C. for two hours at atmospheric pressure and the liberated oxides of nitrogen were estimated iodometrically as mgm. nitric oxide per gram sample. Even when conditions were rigorously standardized, the results depended somewhat on the way the film was dried and upon the percentage of stabilizer present.   Mean values for some of the substances tested are plotted as ordinates in Fig. 5, but all individual determinations are given in Table II, since they often diverged from the mean by more than 10%.   In agreement with others (12, 31), both diphenylamine and Centralite were found to hasten rather than retard the decomposition of the nitrocellulose at 135°C., presumably because their destructive action at this high temperature dominated their stabilization effect.   The value of this accelerated aging test as ordinarily used therefore seemed to rest on the assumption that variable samples of nitro-

cellulose with satisfactory storage properties at ordinary temperatures would display relatively great resistance to destruction by a standard stabilizer at elevated temperatures. The present research, however, abused the test by making the assumption that various good stabilizers at ordinary temperatures would exert the least destructive action at 135°C. on a standard nitrocellulose. The same tacit assumption has been made by others (57). Moreover, although a satisfactory correlation between the Bergmann–Junk–Mayrhofer and storage tests has been claimed (30), such accelerated tests should be carried out at more than one temperature (31) and reliance should be placed on results of several different types of tests, rather than on one alone (61), since the chemical course of the decomposition was not necessarily the same at ordinary and elevated temperatures (25, 52, 55). These considerations suggest that the Bergmann–Junk numbers in Table II are of qualitative or, at best, of semi-quantitative significance, although they may serve to eliminate substances unsuitable as stabilizers.

Some of the differences nevertheless appeared large enough to be attributed to difference in structure. The substitution of 3, 4-dimethoxy or 3-methoxy-4-ethoxy groups in the aromatic rings of Ethylcentralite (Ia → Ic → Id), its benzyl analogue (IId → IIa → IIb), and perhaps in distyryl ketone (IVc → IVa → IVb) markedly increased the Bergmann–Junk number, but the same substitution in dibenzylsuccinamide caused a decrease (IIId → IIIb → IIIc). The substitution of an ethoxyl for a methoxyl group gave poorer results except in the case (IIa → IIb) where the reverse was definitely true. Vanillin gave an unexpectedly favorable value, in view of the fact that phenol in presence of a trace of mineral acid rapidly causes the degradation of cellulose. Methylation of the exposed phenolic group was perhaps slightly deleterious (Va) and this effect was definite after ethylation (Vb). The distyryl ketone series (IV) gave very good results but additional conjugation in similar molecules promoted a tendency toward detonation (Table II, (VIII)).

The abscissas of Fig. 5 record on a grams nitrogen dioxide per gram sample basis the rapid (open circles) and 1000 min. absorption (filled circles) of nitrogen dioxide from carbon tetrachloride by some of the substances studied, the data being derived from Figs. 1 to 4 and from Table II. Reference to the points for substances (IIIa), (IIIc), and (Ib) shows that the three had widely different Bergmann–Junk values but practically the same capacity on a weight basis to absorb nitrogen dioxide from carbon tetrachloride, while by far the highest absorption was possessed by diphenylamine (VI), with an intermediate number. This lack of correlation suggested that the stability test might be influenced by the relative basicities of the substances, and 0.01 molar solutions of (Ia), (IIa), (IIb), and (VI) in 50% aqueous ethanol were accordingly titrated potentiometrically against 0.1 N sulphuric acid. The initial apparent pH values were 7.8, 7.75, 7.75, and 7.65 respectively, and the plots of pH against number of cubic centimeters of added acid were all so similar to that of the solvent (initial pH 7.8) that attempts to determine
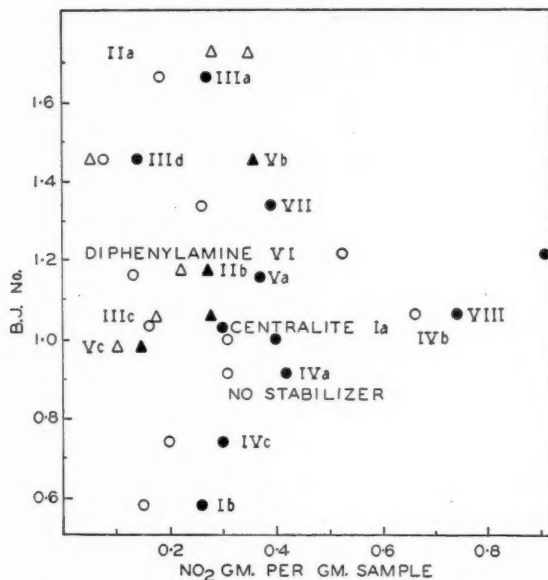
FIG. 5. *Adsorption of nitrogen dioxide by pure sample plotted against Bergmann–Junk numbers (ordinates) observed on standard nitrocellulose film containing 2% of sample. Rapid adsorption in carbon tetrachloride, O; after 1000 minutes, ●. Rapid gaseous adsorption at 42 mm. pressure × 10, △; after five minutes, ▲. For compounds I to IX see Table I.*

relative basicities in this crude fashion were abandoned. Fig. 5 also shows on a tenfold scale some absorptions of gaseous nitrogen dioxide. As already mentioned, these data appeared to be of no theoretical significance.

Table III summarizes results with three arbitrary methods of testing the compatibility of many of the substances in Table I with a dry, technical nitrocellulose containing 12.61% N. Exhaustive tests could not be made owing to lack of material. Method A made use of the fact that the nitrocellulose failed to dissolve or swell obviously when immersed in a standard ethanol–ether mixture, but dissolved completely when an equal weight of Ethyl-centralite was added. This test differentiated fairly well between the various proposed stabilizers. Method B, employing the films cast from acetone for the Bergmann–Junk determinations, was unsatisfactory because the films were almost always of good quality and seemed to differ only in their brittleness. Method C noted the mutual solubility of the proposed stabilizer and the nitrocellulose after the homogeneous melt had cooled for 18 hr. Although the fusion sometimes had to be carried out at more than 100°C. and the results were therefore not always comparable, the test differentiated well between the substances tried. Comparisons of (Ic) and (Id) with (Ia); (IIIb) and (IIIc) with (IIId); (IVa) and (IVb) with (IVc), indicated that substitution of alkoxyl groups tended to improve compatibility with the nitrocellulose, but the trend

TABLE III
COMPATIBILITY WITH NITROCELLULOSE 12.61% N

	(A) Stabilizer 0.3 gm. N.C. 0.3 gm. EtOH–EtOEt (1: 1) 5 cc.	(B) Film from N.C. 5 gm.; stabilizer 0.25 gm. and acetone 50 cc.	(C) Heated 0.05 gm. N.C. and 0.15 gm. stabilizer for 30 min. Examined 18 hr. later
Ia	Good, viscous soln.	Good, clear	100°C. Good, rubbery
Ib		Good, clear	150°C. Good, dark, sticky
Ic		Good, clear	
Id		Good, tough	100°C. Good, hard
If			150°C. Decomp. black
IIa	No swelling	Good, clear	150°C. Hard, dark
IIb	Good, viscous soln.	Good, clear	100°C. Good, hard
IIc	No swelling, immiscible		
IId		Good, tough, clear	100°C. Very good, clear
IIIa		Good, clear	
IIIb		Brittle	100°C. Good
IIIc			150°C. Good, hard
IIId		Brittle	100°C. Poor, hard
IVa	Fair, highly swollen	Brittle	100°C. Poor, hard, brittle
IVb	No swelling		150°C. Poor, black, brittle
IVc	Slight swelling		150°C. Poor, crystallized
IVd		Brittle, insol. in part	200°C. Expl. at 170°C.
Va	Slight swelling	Good, clear	100°C. Very good, rubbery
Vb	Slight swelling	Good, clear	100°C. Poor, crystalline, opaque
Vc	Slight swelling	Good, clear	100°C. Good, few white specks
VI	No swelling, slow discoloration	Good, clear	100°C. Poor, opaque
VIII		Very brittle	100°C. Black, hard
IX			200°C. Expl. at 175°C.

in the benzylureas (IIa) and (IIb) to (IId) was indecisive. Replacement of the 4-methoxyl by the 4-ethoxyl group perhaps improved compatibility with the benzylureas (II) but decreased it with the distyrylketones (IV) and the vanillin series (V). The results with the Ethylcentralites (I) and the benzyl-succinamides (IIIb) and (IIIc) were indefinite in this respect. Tests A and C revealed the poor compatibility of diphenylamine (VI) with the nitrocellulose.

When the behavior of the approved stabilizers, diphenylamine and Centra-lite, is considered, it seems reasonable to conclude that any new stabilizer should meet the following criteria: (a) absorb nitrogen dioxide as avidly as Centralite, (b) cause no more destruction of nitrocellulose in the Bergmann–Junk test than diphenylamine causes, (c) be no less compatible than diphenyl-amine with nitrocellulose, (d) have a melting point no higher than 80°C. A review of Tables II and III with these criteria in mind shows that only the following compounds (Table I) require further consideration as potential stabilizers: IIb, IId, IIIb, IVa, Va. The 10 atom straight chain between the aromatic nuclei of the benzylsuccinamide (IIIb) is of interest because its presence might improve the low-temperature flexibility of nitrocellulose, as plasticizers containing long, normal hydrocarbon units are known to do for polyvinyl chloride films.

The authors wish to emphasize that none of the above work carries the implication that one or more of the substances IIb, IId, IIIb, IVa and Va are in fact practical and safe stabilizers. The results merely suggest that the general properties of the five substances justify a more searching examination of their possible usefulness for this purpose.

Experimental

The following unsaturated ketones were prepared as yellow or orange crystals by the general method of Stobbe and Haertel (48) in which an ethanol solution of the appropriate aldehyde was condensed with acetone in the presence of aqueous sodium hydroxide. Carbon, hydrogen, and alkoxyl analyses were satisfactory in all cases. Di-furfurylidene acetone (VIII), m.p. 57.5°C. (32) and 61°C. (7); found, yield 97% and m.p. 62°C. Distyryl ketone (IVc), m.p. 110°C. (8); found, m.p. 110°C. Di-(3,4-methylenedioxystyryl)-ketone (IVd), m.p. 185°C. (21); found, m.p. 188°C. Di-(3-methoxy-4-ethoxystyryl)-ketone (IVb), m.p. 123°C. (13); found, 40% yield and m.p. 121° to 123°C. Di-(3,4-dimethoxystyryl)-ketone (IVa), m.p. 84°C. (13, 48); found, 38% of canary yellow needles m.p. 79° to 81°C. These needles were reported to have changed to a yellow-brown powder when kept in a sealed tube for a few months (13).

Sym-N,N'-Diethyl-N,N'-dibenzylurea (IId)

Distilled N-ethylbenzylamine, which boiled at 196° and 80°C. under pressures of 760 mm. and 4 mm. of mercury, respectively, was prepared as previously described (20). A solution of 16 gm. in 100 cc. of dry benzene, 4.5 gm. of anhydrous sodium carbonate, and 12.5 cc. of a 20% solution of phosgene in dry benzene were heated together, with stirring and under reflux. The redistilled halogen-containing product, 3.7 gm. of light yellow oil, was heated for a further four hours with 2.54 gm. of ethylbenzylamine and 4 gm. of sodium carbonate. Dilution with 50 cc. of ether and cautious decantation removed a suspension of fine white flakes (shown to be 1.5 gm. of crude N-ethylbenzylamine hydrochloride) from the sodium carbonate, and concentration of the filtrate left the desired substance as a pale yellow oil that soon crystallized. The melting point was 56°C., unchanged by recrystallization from petroleum ether. N,N'-Diethyl dibenzylurea was very soluble in ethanol, soluble in ether, and sparingly soluble in petroleum ether and acetone. The yield of about 30% could doubtless be improved (23, 24). Calc. for $C_{19}H_{24}N_2O$: N, 9.46%. Found: N, 9.39, 9.41% (micro-Kjeldahl by J. L. Keays).

Sym-N,N'-Diethyl-N,N'-di-(3,4-dimethoxybenzyl)-succinamide (IIIb)

A solution of 5.4 gm. of N-ethyl-3,4-dimethoxybenzylamine (18) in 75 cc. of benzene was stirred with 4.5 gm. of powdered, anhydrous potassium carbonate while a solution of 1.7 cc. of succinyl chloride (20) in 10 cc. of

benzene was added rather rapidly at room temperature. After four hours of stirring, the mixture was filtered and the filtrate was washed in succession with aqueous sodium carbonate, dilute hydrochloric acid, and water. None of the brown color was removed from the benzene layer by these washings. The residue obtained by evaporation of the benzene was taken up in 30 cc. of ether, some undissolved tar being rejected, and, after clarification with absorbent carbon, the solution, now 15 cc., was poured into 75 cc. of low-boiling petroleum ether. The pale yellow, very viscous oil which separated was freed of solvent in high vacuum at 100°C. Calc. for $C_{26}H_{26}O_6N_2$: N, 5.98%. Found, N, 5.93%.

The substance was high-boiling and all attempts to crystallize it failed.

### N-Ethyl-N-propionyl-3,4-dimethoxybenzylamine (VII)

A solution of 1.7 cc. of propionyl chloride in 10 cc. of benzene was added dropwise, with shaking and cooling, to 3.0 gm. of N-ethyl-3,4-dimethoxybenzylamine (18) dissolved in 30 cc. of benzene. A white precipitate rapidly formed. After standing for an hour, the addition of 15 cc. of water dissolved this precipitate and the solution, plus excess sodium carbonate, was used to extract the benzene layer. The aqueous layer was back-extracted with benzene, and evaporation of the combined benzene liquors left an oil which was distilled at 180° to 190°C. (2 mm. pressure). The propionamide was a rather fluid, slightly yellow oil that could not be crystallized. Calc. for $C_{14}H_{21}O_3N$: N, 5.6; OCH_3, 24.6%. Found: N, 5.5, 5.6; OCH_3, 23.4, 23.6%.

Adsorption of Nitrogen Dioxide from Solution

About 25 cc. of distilled nitrogen dioxide (17) was redistilled from phosphorus pentoxide at room temperature into a receiver cooled by acetone and solid carbon dioxide. All-glass equipment was used. The white, crystalline product was allowed to melt and was stored in a small flask fitted with a stopcock. When required, about 4.4 cc. (6.6 gm.) was dissolved in 1.2 liters of reagent grade carbon tetrachloride which had been dried over anhydrous calcium chloride and redistilled. This approximately 0.12 M stock solution was stored in the refrigerator and was stable for days.

A special 50 cc. burette, graduated to 0.01 cc. and equipped at the upper end with a ground-glass joint and stopper, was filled to the 20 cc. mark with the stock solution. The test substance, exactly 0.375 millimoles, was then dissolved in about 20 cc. of carbon tetrachloride; the solution was introduced into the burette and the volume of the mixture was quickly adjusted to the 50 cc. mark with more of the pure solvent. Thorough mixing was brought about by inverting the stoppered burette end over end at least 10 times, and zero time was taken as when the mixing began. At various times thereafter, 5 cc. aliquots were discharged into small separatory funnels containing 2 cc. of 50% aqueous sodium acetate previously neutralized to phenolphthalein. After closing the funnels with rubber stoppers, the contents were occasionally swirled

for at least 15 min., since trial showed that shorter periods gave low and variable results. Water, 25 cc., was then added and after a further five minutes for phase separation the bulk of the carbon tetrachloride layer was removed. The acetic acid in the aqueous layer was titrated with 0.01 N barium hydroxide to a phenolphthalein end point and the amount of nitrogen dioxide calculated from the equation

$$H_2O + 2\ NO_2 + 2\ CH_3COONa \rightarrow 2\ CH_3COOH + NaNO_2 + NaNO_3.$$
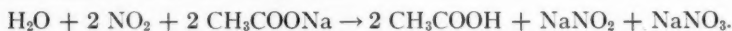
One cubic centimeter of 0.01 M alkali corresponded to 0.2 millimole or 0.92 mgm. of nitrogen dioxide.

Blank estimations showed that the original nitrogen dioxide content was 1.91 mgm. per cc. or 41.8 millimoles per liter, and after two days in the burette the concentration found was 1.87 mgm. per cc. Since decrease in concentration was negligible during the 1000 min. the experiments lasted, the consumption of nitrogen dioxide by the test samples was found by subtracting the residual titer from the blank. The results are summarized in Figs. 1 to 5 and in Table II. Multiple runs were made with closely concordant results on many of the compounds.

Preparation of Nitrocellulose Films

A dope, free of air bubbles and made from 5 gm. of technical nitrocellulose (N, 12.61%, dried *in vacuo* over phosphorus pentoxide), 0.25 gm. of the proposed stabilizer, and 50 cc. of acetone, newly distilled from potassium permanganate, was poured into a thoroughly clean petri dish of 9 cm. diameter and the solvent was allowed to evaporate at room temperature. Films so prepared were, when necessary, removed after adding water and were usually transparent and smooth, although the surfaces of several were distorted and contained opaque areas. This mishap seemed to be caused by uncontrolled temperature or humidity factors because it tended to occur with an entire set of films prepared with different stabilizers on the same day. Unless otherwise noted, all films were dried at 55°C. for 48 hr. before use. Samples of 2 gm. or less were cut into 1 cm. squares and submitted to the Mayrhofer modification (33) of the Bergmann–Junk test.

Compatibility Tests

Method A.—Nitrocellulose (N, 12.61%), 0.3 gm., 5 cc. of ether–ethanol (1:1) and 0.3 gm. of the substance to be tested were shaken together for one minute and then allowed to stand, the immediate appearance of the nitrocellulose being noted. In addition to the observations in Table III, 0.3 gm. samples of dibutyl phthalate, benzyl acetate, and ethyl succinate resulted in viscous, opaque solutions; cyclohexanone, *p*-nitroaniline, cinnamic amide, cinnamic acid, guaiacyl acetone, and urea gave uniform translucent gels; while guaiacol, anisole, β-phenylethanol, resorcinol, phenol and 4-*n*-propylphenol produced no obvious change in the nitrocellulose–ether–alcohol system.

Method C.—Preliminary tests showed that 0.05 gm. of nitrocellulose (12.61% N) and 0.15 gm. of Ethylcentralite gave a completely translucent gel when mixed in a small test tube and heated at 80° to 90°C. for 30 min. More than 0.15 gm. of the stabilizer gave gels from which the excess soon crystallized, and with less the formation of gel was incomplete. The above amounts were adopted for the tests recorded in Table III, the temperature of heating being increased from 100°C. to 150°C. or 200°C. only when necessary to melt the substance.

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THE THERMODYNAMIC FUNCTIONS OF HYDROGEN PEROXIDE[1]

By Paul-A. Giguère

Abstract

Using structural data and vibrational frequencies measured recently, the thermodynamic functions of gaseous hydrogen peroxide were calculated by the statistical method over the range 298.16 to 1500°K. at 100° intervals. Some uncertainty results from the lack of accurate information on the potential barrier hindering free rotation of the OH groups in the molecule. The equilibrium constants of a few important reactions involving hydrogen peroxide were also calculated from existing data on the heat of decomposition and the heat of dilution.

During the last decade, concentrated hydrogen peroxide has gained considerable importance as the result of its use either in liquid fuel mixtures or as a convenient source of gases at high pressures and yet at moderate temperatures. An exact knowledge of its thermodynamic properties is therefore desirable. Because of its unstability and the difficulty of obtaining it in the pure state the thermochemical data available on this compound are relatively scanty. For the same reasons the measurement of its third law entropy would present numerous experimental difficulties. In that connection one might expect hydrogen peroxide to retain residual entropy at low temperatures owing to the existence of strong hydrogen bonds and of two tautomeric forms of the molecule (9). However, a recent investigation of the crystal structure by means of X-rays has shown that such is not the case (8). As to the reactions of hydrogen peroxide, they are so irreversible at ordinary temperatures that their equilibrium constants cannot be determined directly, although Lewis and Randall (7), using a rather involved schema, succeeded, more than 30 years ago, in obtaining a value of the free energy of formation, -24.73 kcal. per mole at 25°C., which is remarkably accurate.

The statistical method is therefore the only possibility in the present case. Two such calculations of the thermodynamic functions of hydrogen peroxide have been published up to now. The first one, by Zeise (25), was based essentially on the results of the Raman spectrum investigations of Simon and Fehér (19–21). The vibrational frequencies he used were fairly correct but the moments of inertia were appreciably different from those obtained from electron diffraction data (5) and from the rotational structure of two overtone infrared bands (4, 26). In addition, owing to an error in the choice of the symmetry number, 1 instead of 2, his values of the free energy function are too high by $R \ln 2$. On the other hand Mickley (13) based his calculations on the spectroscopic results of Bailey and Gordon (1). The assignments made by these authors have been found incorrect, specially as regards the frequency of the torsional oscillation. A recent investigation of the infrared spectrum

of hydrogen peroxide vapor has provided new data which warrant a recalculation of the thermodynamic properties. Because of the remaining uncertainty as to the barrier restricting rotation of the OH groups in the molecule the present results cannot be considered as definitive. A review of the existing thermochemical data, as well as the calculated heat and free energy of formation and of decomposition of hydrogen peroxide as a function of temperature, is also presented for convenience.

Thermodynamic Functions

The structural and spectroscopic data used for these calculations are summarized in Table I. They are based on the model of Penney and Sutherland (15, 16), which has been confirmed repeatedly. The fundamental frequencies were obtained from the recent infrared investigation (4) and the Raman spectrum measured by Fehér (2). The frequencies of ν_1 and ν_5 have been taken as equal, i.e., the observed OH frequency at 3590 cm.$^{-1}$ was given a statistical weight of 2 although, strictly speaking, these two levels cannot be degenerate, as they belong to different symmetry classes. The value 1320 cm.$^{-1}$ for ν_2 was obtained by applying to the Raman frequency in the liquid, 1420 cm.$^{-1}$, an appropriate correction for the liquid–vapor shift (1350–1255 cm.$^{-1}$). The accuracy of these figures is not very high since none of the fundamental

TABLE I

MOLECULAR DATA FOR HYDROGEN PEROXIDE

Fundamental vibrations	Frequency, cm.$^{-1}$
$\nu_1\ (a)$	3590
$\nu_2\ (a)$	1320
$\nu_3\ (a)$	877
$\nu_4\ (a)$	500
$\nu_5\ (b)$	3590
$\nu_6\ (b)$	1255

Structural parameters

$r_{O-O}\ = 1.48\ Å$
$r_{O-H}\ = 0.98\ Å$
$\theta_{H-O-O} = 102°$
$\phi\ (azimuthal) = 110°$

Moments of inertia

$I_A\ =\ 2.78_6 \times 10^{-40}$ gm. cm.^{2}
$I_B\ =\ 32.9$ " "
$I_C\ =\ 34.8$ " "
$I_{red}\ =\ 0.696$ " "

bands of hydrogen peroxide have been studied yet under high dispersion. However, the resulting inaccuracy in the thermodynamic functions is not serious because of the small contribution of the vibrational levels.

Such is not the case of ν_4, the torsional oscillation about the O–O bond. The only information available on this oscillation is a broad absorption band observed in the infrared spectrum of the liquid. Its frequency was first reported as 550 cm.$^{-1}$ (4) but a more recent investigation has revealed that it centers rather around 600–620 cm.$^{-1}$.* From this value one must subtract the shift due to molecular association in the liquid which, for lack of a more definite indication, may be taken as equal to that for the bending frequencies, i.e., of the order of 100 cm.$^{-1}$ If correct, the frequency at about 500 cm.$^{-1}$ in the vapor would correspond to a potential barrier of 4–5 kcal. per mole. A somewhat higher value, 6 kcal. per mole for the lower of the two barriers, was obtained from quantum mechanical calculations by Penney and Sutherland (15, 16). For the present purpose it was assumed that the restricting barrier was of the form

$$V = \frac{1}{2} V_0 (1 - \cos 2\theta)$$

with $V_0 = 5$ kcal. per mole. The contribution of this level was calculated by means of the tables of Pitzer and Gwinn (17) with the reduced moment of inertia taken as $I_{red.} = \frac{1}{4} I_A$. This approximation was deemed permissible, considering the uncertainty of the value of V_0 and the small angle between the OH group axis and the small axis of the molecule. The usual approximations, "Harmonic Oscillator – Rigid Rotator" were made and the spin contribution of the two hydrogen atoms were neglected. The vibrational contributions were obtained from the tables of Schumann and Schwartz (given in (23)). All the fundamental constants used were those from the Tables of the National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties" (14).

The well known equations (24) for the thermodynamic functions of one mole of the ideal gas at 1 atm. pressure are as follows in the case of hydrogen peroxide:

$$(H^0 - H_0^0) = RT \left(4 + \sum \frac{x}{e^x - 1} \right),$$

$$-\left(\frac{F^0 - H_0^0}{T} \right) = R \left(\frac{3}{2} \ln M + 4 \ln T + \frac{1}{2} \ln (I_A I_B I_C) - \ln \sigma \right.$$
$$\left. - \sum \ln (1 - e^x) + 129.522 \right),$$

$$C_p = R \left(4 + \sum \frac{x^2 e^x}{(e^x - 1)^2} \right),$$

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* *This revised value confirms the results of an infrared study of crystalline and supercooled liquid hydrogen peroxide made independently (22).*

where M is the molecular weight, 34.015, σ the symmetry number for the over-all rotation, 2 (considering the torsional oscillation as frozen), and $x = 1.438 \, \omega/T$, ω being the various fundamental frequencies, except ν_4, in wave numbers. The results of the calculations are presented in Table II after the fashion adopted in the Tables of the National Bureau of Standards. The numbers given in parentheses represent the functions exclusive of the internal rotation contribution: they are given here for convenience in recalculating more exact thermodynamic functions when additional information on that level becomes available. They also illustrate its relative importance at various temperatures. As is customary for such calculations the results are reported with greater accuracy than is justified by the different assumptions made.

TABLE II

THERMODYNAMIC FUNCTIONS FOR GASEOUS HYDROGEN PEROXIDE AT 1 ATM.

T, °K.	$-\left(\dfrac{F^0 - H_0^0}{T}\right)$, cal./deg./mole		$\dfrac{H^0 - H_0^0}{T}$, cal./deg./mole		S^0, cal./deg./mole		C_p^0, cal./deg./mole		$H^0 - H_0^0$ cal./mole	
298.16	(45.33)	45.53	(8.12)	8.65	(53.45)	54.18	(8.79)	10.22	(2421)	2579
300	(45.38)	45.59	(8.13)	8.66	(53.51)	54.25	(8.81)	10.25	(2439)	2598
400	(47.75)	48.16	(8.41)	9.23	(56.16)	57.39	(9.72)	11.54	(3364)	3692
500	(49.67)	50.28	(8.76)	9.80	(58.43)	60.08	(10.58)	12.58	(4380)	4900
600	(51.29)	52.11	(9.12)	10.33	(60.41)	62.54	(11.30)	13.35	(5472)	6198
700	(52.73)	53.74	(9.48)	10.80	(62.21)	64.54	(11.90)	13.94	(6636)	7560
800	(54.01)	55.22	(9.82)	11.22	(63.83)	66.44	(12.42)	14.39	(7856)	8976
900	(55.20)	56.56	(10.14)	11.60	(65.34)	67.16	(12.89)	14.80	(9126)	10440
1000	(56.27)	57.80	(10.43)	11.94	(66.70)	69.74	(13.32)	15.14	(10430)	11940
1100	(57.28)	58.94	(10.71)	12.23	(67.99)	71.17	(13.70)	15.45	(11781)	13453
1200	(58.22)	60.01	(10.97)	12.51	(69.19)	72.52	(14.06)	15.73	(13164)	15012
1300	(59.13)	61.05	(11.23)	12.77	(70.36)	73.82	(14.38)	15.97	(14599)	16601
1400	(59.96)	61.99	(11.47)	13.01	(71.43)	75.00	(14.68)	16.23	(16058)	18214
1500	(60.75)	62.88	(11.69)	13.24	(72.14)	76.12	(14.94)	16.45	(17535)	19860

NOTE:—*The numbers in parentheses do not include the contribution of internal rotation.*

Heat and Free Energy of Formation

The determination of the heat and free energy of formation of hydrogen peroxide is, of necessity, based on its measured heat of decomposition. The available data on this quantity are summarized in Table III. By correlating the results of Matheson and Maass (11) with those of Roth, Grau, and

TABLE III

HEAT OF DECOMPOSITION OF LIQUID HYDROGEN PEROXIDE

Temperature, °C	Conc. H_2O_2, wt. %	ΔH measured, kcal./mole	Estimated precision, cal.	Ref.
20	97.15	−23.42	±20	(11)
20	38.05	−22.73	±20	(11)
20	30.00	−22.70	±30	(18)
20	15.83	−22.66	±30	(18)
25	∼ 0.1	−22.59	±20	(3)
25	99	−24.30		(12)

Meichsner (18) on the heat of decomposition and the heat of dilution of aqueous solutions of hydrogen peroxide Mickley (13) arrived at a recommended value of $-23{,}470$ cal. per mole at 20°C. for the heat of the reaction:

$$H_2O_2(l) = H_2O(l) + \tfrac{1}{2} O_2(g).$$
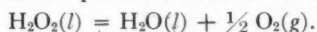
The results obtained since by Fontana (3) are in complete agreement with the above. As to the value -24.30 kcal. deduced by Médard (12) from measurements at constant volume in a calorimetric bomb, it will not be considered here, for lack of details on the experiment and on its estimated precision.

In order to arrive at the heat of decomposition of gaseous hydrogen peroxide at 20°C. use was made of the recent vapor pressure measurements of Kavanagh (6), which are believed to be somewhat more accurate than the previous ones of Maass and Hiebert (10). (The author is very grateful to Dr. G. M. Kavanagh, for permission to quote this datum prior to publication.) By means of the Clapeyron–Clausius equation the heat of vaporization was found to be 12.57 kcal. per mole at 20°C., that for water being 10.54 kcal. per mole. From these the heat of the reaction

$$H_2O_2(g) = H_2O(g) + \tfrac{1}{2} O_2(g)$$
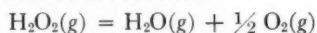
is therefore -25.50 kcal. per mole at 20°C. The same value can be used at 25°C. since the enthalpy function of hydrogen peroxide (Table II) shows that the difference in this quantity at the two temperatures is entirely within the limits of accuracy of the calorimetric measurements. From the heat of formation of water vapor at 25°C., -57.7976 kcal. per mole (14) Series I, Table No 8a, that of gaseous hydrogen peroxide is found to be -32.30 kcal. per mole at the same temperature. Combining this value with the appropriate thermodynamic functions for hydrogen peroxide (Table II) and those for oxygen and hydrogen (14) Series III, Tables No 7 and 8, the heat of formation, free energy of formation, and logarithm of the equilibrium constant for the formation of gaseous hydrogen peroxide were computed as a function of temperature (Table IV).

TABLE IV

HEAT, FREE ENERGY, AND EQUILIBRIUM CONSTANT
OF FORMATION OF GASEOUS HYDROGEN PEROXIDE

$T,$ °K.	$\Delta H^0,$ kcal./mole	$\Delta F^0,$ kcal./mole	$\mathrm{Log_{10}}K$
0	-30.79	-30.79	
298.16	-32.30	-24.55	17.99
300	-32.31	-24.50	17.84
400	-32.62	-21.84	11.93
500	-32.84	-19.12	8.35
600	-33.00	-16.35	5.95
700	-33.12	-13.58	4.24
800	-33.21	-10.78	2.94
900	-33.27	$- 7.97$	1.93
1000	-33.31	$- 5.16$	1.13
1100	-33.36	$- 2.32$	0.46
1200	-33.39	$+ 0.50$	$- 0.09$
1300	-33.40	3.30	$- 0.55$
1400	-33.41	6.15	$- 0.96$
1500	-33.40	8.99	$- 1.31$

Heat and Free Energy of Decomposition

By far the most important reaction of hydrogen peroxide is that in which it decomposes spontaneously into water and gaseous oxygen. The data in Table V were obtained from the appropriate thermodynamic functions of water vapor and of oxygen (14) Series III, Tables No. 7 and 8. They fully confirm the conclusion of Lewis and Randall (7) that the decomposition is essentially complete up to 1500°K. and even at much higher temperatures, as may be judged by extrapolation.

TABLE V

HEAT, FREE ENERGY, AND EQUILIBRIUM CONSTANT
OF DECOMPOSITION OF GASEOUS HYDROGEN PEROXIDE
INTO WATER VAPOR AND OXYGEN

T, °K.	ΔH^0, kcal./mole	ΔF^0, kcal./mole	$\mathrm{Log}_{10}K$
0	−26.32	−26.32	
298.16	−25.50	−30.08	22.04
300	−25.49	−30.12	21.94
400	−25.42	−31.62	17.27
500	−25.43	−33.24	14.53
600	−25.50	−34.80	12.67
700	−25.58	−36.33	11.33
800	−25.68	−37.86	10.34
900	−25.79	−39.38	9.56
1000	−25.90	−40.87	8.93
1100	−26.00	−42.37	8.41
1200	−26.11	−43.86	7.99
1300	−26.22	−45.30	7.61
1400	−26.33	−46.79	7.30
1500	−26.44	−48.25	7.02

TABLE VI

HEAT, FREE ENERGY, AND EQUILIBRIUM CONSTANT
OF DECOMPOSITION OF GASEOUS HYDROGEN
PEROXIDE INTO HYDROXYLS

T, °K.	ΔH^0, kcal./mole	ΔF^0, kcal./mole	$\mathrm{Log}_{10}K$
0	50.8	50.8	
298.16	52.42	42.41	−31.08
300	52.44	42.36	−30.85
400	52.76	39.03	−21.32
500	52.96	35.45	−15.49
600	53.07	31.93	−11.62
700	53.13	28.41	− 8.86
800	53.14	24.88	− 6.79
900	53.11	21.35	− 5.18
1000	53.06	17.82	− 3.89
1100	53.02	14.28	− 2.84
1200	52.97	10.76	− 1.96
1300	52.90	7.27	− 1.22
1400	52.83	3.74	− 0.58
1500	52.75	0.22	− 0.03

Since the mechanism of decomposition of hydrogen peroxide involves, as the primary step, the breaking of the O–O bond it was thought of interest to compute the heat and free energy of the reaction

$$H_2O_2(g) = 2 \, OH(g)$$

from the available thermodynamic functions of the hydroxyl radical (14) Series III, Table No 8. As may be seen in Table VI this reaction is always strongly endothermic, but the free energy change decreases rapidly with increasing temperature.

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Résumé

On a calculé par la thermodynamique statistique l'entropie et les différences d'enthalpie et d'énergie libre du peroxyde d'hydrogène à l'état gazeux à intervalles de 100° entre 300° et 1500°K. Ces calculs ont été faits à partir des données actuelles sur la structure et les vibrations fondamentales de la molécule. On a également calculé les constantes d'équilibre et les chaleurs de réaction pour la formation et la décomposition du peroxyde d'hydrogène pur à ces températures. Le manque de données suffisamment précises sur la fréquence d'oscillation relative des deux groupes OH dans la molécule introduit une légère incertitude dans les résultats.

AN APPARATUS FOR THE LOW TEMPERATURE FRACTIONATION OF SMALL GAS SAMPLES[1]

By D. J. Le Roy

Abstract

A simple apparatus has been developed for fractionating polycomponent gas samples at temperatures at which the take-off pressure is of the order of 0.5 mm. Fractions as small as 0.06 cc. of gas have been isolated and their vapor pressures determined.

In the fractionation of a polycomponent liquid the relative volatilities of the components are of paramount importance. In general, the nearer the relative volatility, α, of any pair of components is to unity the greater is the number of theoretical plates required for their separation. In dealing with small gas samples the limiting factor is the hold-up of the column, which increases with the number of theoretical plates. A number of methods have been devised to overcome this difficulty by taking advantage of the fact that the relative volatility of two components is an inverse function of the temperature.* In many cases satisfactory separations can be made with a single "plate", provided the vapor pressure of the more volatile component is less than one mm.

The apparatus used by Ward (8), which was a modification of an earlier apparatus of Shepherd and Porter (6), consisted of a train of several traps arranged in order of decreasing temperature. On passing a gas sample through these a partial fractionation takes place in which the higher boiling components are condensed in the warmer traps, the lower boiling components in the colder traps. If, at the temperature of the coldest trap, the vapor pressure of the lowest boiling component is less than 1 mm., practically all of this component may be pumped off and measured without its being contaminated with any appreciable amount of the other materials. The lower limit of the pressure to which pumping is permissible will be determined by the relative volatility of the two lowest boiling components. After the first component is removed, the temperature of each trap is raised and the second component pumped off and measured. Generally the relative volatility of olefins and paraffins of the same carbon number is too close to unity to permit their separation, but Ward was able to separate a mixture of several hydrocarbons into fractions according to carbon number. Noncondensable gases such as hydrogen, methane, and carbon monoxide are pumped off with the coldest trap at the temperature of liquid air or liquid nitrogen.

If the vapor pressures of two pure substances, X and Y, are given by the simple equation, log $p = -A/T + B$, then $\log \alpha = -(A_X - A_Y)/T + (B_X - B_Y)$, where $\alpha = (p_X/p_Y)_T$.

Boomer, Gillies, and Hugill (3) simplified the method of Ward by using a single metal column down which there was a temperature gradient; the coldest point was at the bottom.   On entering the column the gas sample is made to pass over a series of cone-shaped vanes distributed over the whole length of the column.   The higher boiling components collect at the top of the column, the lower boiling components at the bottom.   The various fractions are removed from the bottom of the column.   Less manipulation is required than for the Ward still, since it is only necessary to control the temperature of a single column.

Although very satisfactory results have been obtained with the Boomer still, its construction can be undertaken only by a competent machinist, and when a number of columns are required the cost becomes an important factor. During the past four or five years a greatly simplified version of this column has been developed and used in the separation of fractions as small as 1 cc. or less of gas.   The success of this column in a number of laboratories has made it desirable to describe it in some detail.

The general construction of the column is indicated in Fig. 1.   The central trap, into which the gas is condensed, is made from a 12 mm. O.D. tube B and a 6 mm. O.D. tube A.   The column is ring-sealed at R to a jacket tube C which is provided with a 29/42 standard taper joint.   Tube C is 25 mm. O.D. The length of the column below the ground joint is approximately 35 cm.
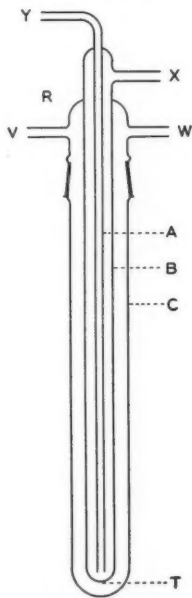

FIG. 1.   *The fractionating column.*

A copper–constantan thermocouple, made from No. 30 B. and S. enameled wires, is fastened to the bottom of the column at T with Scotch tape. Three similar thermocouples are fastened farther up the tube B at intervals of 2, 8, and 14 cm. from the bottom. The outer surface of B is then wound with strips of lead or silver foil 0.003 in. thick and $1\frac{1}{2}$ in. wide. The foil is pressed tightly around the bottom of the tube to ensure a good thermal contact, and extends up to a point just below the level of the ground joint. The metal foil is then wound with a layer of woven glass tape 1 in. wide, care being taken to cover the bottom of the trap as well as the sides; the tape may be secured at the free end and around the bottom of the trap by sewing it together with glass thread.

The heating coil, of No. 30 B. and S. enameled constantan wire, is wound over the glass tape. To avoid the possibility of short circuits the lead-in wire of the heater is brought to the bottom of the trap through a woven glass insulating tube. The turns of the heating coil are usually evenly spaced at intervals of about 10 mm.; in some cases the distance between the turns has been varied continuously from about 10 mm. at the bottom of the column to 6 or 7 mm. at the top, but no particular advantage appeared to be gained in this way. The resistance of the heater is of the order of 10 to 15 ohms. The thermocouple and heater wires are brought out through the tube W, into which they are sealed with Dekhotinsky cement.

The space between the tubes B and C serves as a thermal insulator between the column and the external cooling bath of liquid air, liquid nitrogen, or dry ice – acetone. In the earlier models this space was filled with windings of asbestos paper and left open to the atmosphere. However, under these conditions moisture condensed around the column and the increased thermal conductivity increased the liquid air consumption. It was impossible to use liquid nitrogen as the cooling medium with this arrangement because of the condensation of atmospheric air. In the present model the space between B and C is connected through V to the vacuum system and a manometer. Sufficient insulation is provided by using a pressure of a few millimeters of air; the pressure used will affect the temperature gradient in the column and can be varied according to the temperature range over which the column is to be used.

In the analysis of a sample the tube C is immersed to a depth of about 28 cm. in liquid air or liquid nitrogen. The temperature of the column is quickly lowered to that of the cooling medium by increasing the air pressure between B and C. The sample is admitted to the column and the noncondensable gas is removed through V and collected in a calibrated volume by means of a Toepler pump (see Fig. 2). In some cases the Toepler pump has been supplemented by a mercury diffusion pump to reduce the time taken for an analysis when the sample is originally contained in a volume of a liter or more. The noncondensable fraction is assumed to be removed when the pressure in the column has been lowered to 10^{-2} or 10^{-3} mm. The pressure in the jacket is
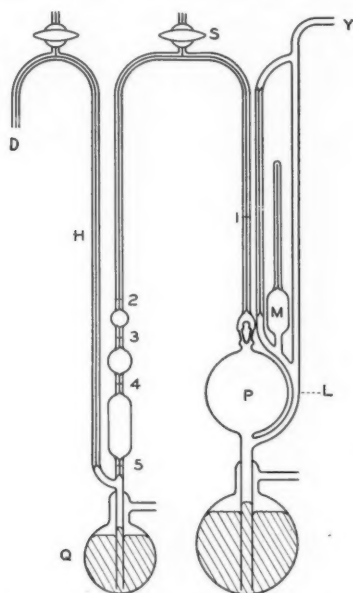
FIG. 2.   *McLeod gauge, Toepler pump, and calibrated volumes.*

then reduced and the column heater turned on.   The voltage across the heater is gradually increased until the pressure in the column has risen to about 0.5 mm.   During this interval a number of temperature (coldest junction) and pressure readings are taken and compared with the vapor pressure data of likely components.   Using an initial take-off pressure of about 0.5 mm. and a final pressure at the end of a cut of 10^{-2} to 10^{-3} mm., it is possible to separate a mixture of hydrocarbons according to their carbon number.   With care it is even possible to separate a C_2 cut into fractions which are predominately ethane, ethylene, or acetylene, although olefin (5) and acetylene (2) determinations are always made on these fractions.

The particular take-off pressure (or temperature) used for any constituent will depend, to a certain extent, on the relative volatility of the other constituents.   In some cases take-off pressures as low as 0.1 mm. have been used, to reduce the contamination of the fraction by the next higher boiling constituent.   On the other hand, the take-off pressure for, say, ethylene in a mixture containing nothing between ethylene and butene could be as high as 1 mm. or more.

The method used to follow the pressure in the column and to remove the various fractions and measure their volumes is shown in Fig. 2.   The pressure in the column is measured on the small McLeod gauge M.   In the reading of these pressures the mercury level is not allowed to go below L.   When the

required take-off pressure is obtained the fraction is pumped into one of the calibrated volumes, 1-2, 1-3, 1-4, or 1-5, by the Toepler pump P. The particular calibrated volume used is determined by the pressure on the mercury reservoir Q. The upper part of the tube H is connected through a stopcock to the manifold of the high vacuum system; the pressure of the gas in the calibrated volume is therefore equal to the difference between the mercury level at 2, 3, 4 or 5, and the level in the tube H. The stopcock S leads to a device, to be described below, for separating hydrogen from other noncondensable gases. In the measuring of the volume of a fraction the level of the mercury above the float valve of the Toepler pump is set at 1. In one modification of the apparatus the mercury-seal feature of the float valve is retained, but the use of an iron core and solenoid make it possible to release the mercury from the seal and to pump the gas, without restriction, into the calibrated volume.

If chemical analysis of a fraction is not required it is removed from the calibrated volume by lowering the pressure in the reservoir Q and evacuating this volume through H and the manifold. Alternatively, by using the device shown in Fig. 3 the fraction may be collected at atmospheric pressure in an inverted test tube over mercury for analysis by the Blacet–Leighton method (1). The height of the capillary tubes E and F is made greater than atmospheric height so that mercury will not be drawn from the pneumatic trough K to the reservoir M when the latter is evacuated during the pumping operation in which gas is transferred from the calibrated volume (Fig. 2) to J. By applying a pressure in excess of atmospheric to the reservoir M the gas in J
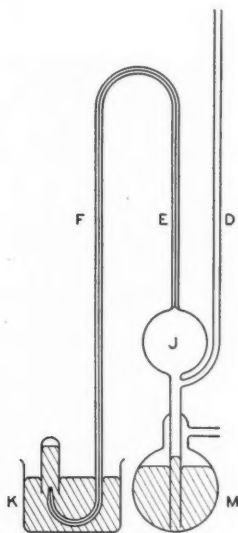

FIG. 3. *Toepler pump for collecting gas samples at atmospheric pressure.*

may be forced over into the inverted test tube in the pneumatic trough K. Only a small quantity of mercury is transferred from M to K during this operation.   To avoid the transfer of mercury from M to Q (Fig. 2) the height of tube D must be greater than that of E or F.

In many of the analyses carried out with this apparatus the noncondensable gas was a mixture of hydrogen and methane.   In these cases the total non-condensable gas, or an aliquot, was first measured in one of the calibrated volumes; the hydrogen was then removed through a hot palladium tube connected at S (Fig. 2).   The arrangement of the palladium tube is shown in some detail in Fig. 4.   It was made in the form of a thimble $2\frac{1}{2}$ in. long and 3/16 in. outside diameter with a wall thickness of 0.008 in.   At the open end it was platinum soldered to a platinum funnel made from 0.003 in. sheet. The funnel extended up into the palladium tube a distance of 1/16 in.   The large end of the funnel was $\frac{1}{2}$ in. in diameter and had a feather edge.   After fusing a layer of soft glass around the edge it was sealed to the soft glass jacket as shown.
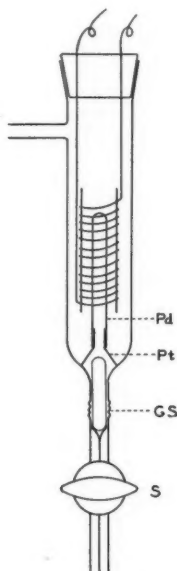

FIG. 4.   *Palladium tube for removing hydrogen from other noncondensable gases.*

The connection between the palladium tube and the stopcock S was made through a soft glass-to-Pyrex graded seal GS.   Dead space was reduced by inserting a glass rod in the tube above S.   The upper part of the palladium tube was heated electrically to about 350°C. by means of a coil of resistance wire wound around a short length of quartz tubing.   Care must be taken not to overheat the palladium, particularly in the presence of oxygen.   The

jacket is evacuated continuously as the hydrogen diffuses through. To ensure that all the hydrogen comes in contact with the palladium the mercury level in the calibrated volumes is raised and lowered a number of times during the diffusion process. To measure the residual gas accurately the mercury level is lowered to point 5 (Fig. 2), the stopcock S is then closed and the amount of gas between 1 and 2, 3 or 4 noted; this is then corrected for the small amount remaining in the palladium tube system.

This system of gas analysis has been used for a wide variety of mixtures. In Fig. 5 are shown vapor pressure data obtained by Lee and Le Roy (4) in the course of the analysis of mixtures of hydrogen, methane, hydrogen chloride, methyl chloride, and ethylene chloride. The reproducibility of the data is shown by the fact that the points for methyl chloride were drawn from the results of three different analyses. In a number of experiments the volume of ethylene chloride was about 0.06 cc. of gas at N.T.P., but despite this small amount the vapor pressures obtained agreed reasonably well with the values obtained in the analysis of a sample containing 0.93 cc. of ethylene chloride. In Fig. 5 both types of data are compared with the vapor pressures obtained with a sample of pure ethylene chloride having a volume of 2 cc. of *liquid*. It should be pointed out that the thermocouples used in this work were not calibrated, since it was not our desire to obtain accurate low temperature vapor pressure data. The method recently devised by Tickner and Lossing (7) would appear to be well adapted for extending the range of accurate vapor pressure data into the previously neglected region of interest in low temperature fractionation.
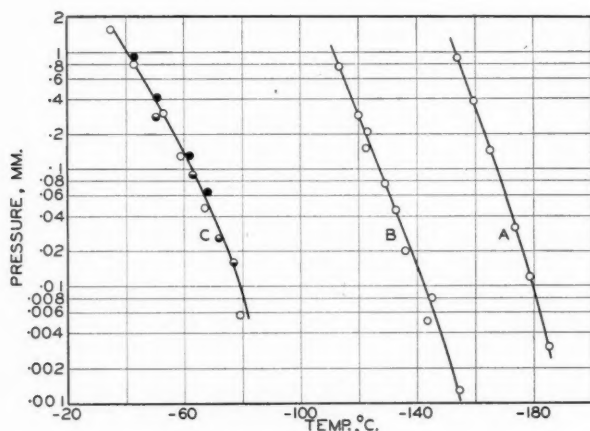

FIG. 5. *Vapor pressures determined during the fractionation of samples containing hydrogen, methane, hydrogen chloride, methyl chloride, and ethylene chloride. A—hydrogen chloride; B—methyl chloride; C—ethylene chloride. For curve C:* ◐ *= 0.06 cc. of gas,* ○ *= 0.93 cc. of gas,* ● *= 2 cc. of liquid.*

In Table I are shown duplicate analyses of a known mixture, obtained by Mr. G. R. Hoey during a test of one of the columns.

TABLE I

FRACTIONATION OF A SAMPLE OF KNOWN COMPOSITION

	Ethane %	Propylene %	n-Butane %	Volume of sample,* cc.
Known composition	37.4	33.7	28.9	8.2
Found	38.8	33.8	27.3	1.1
Found	38.2	33.8	28.0	1.0

*At 25°C. and 760 mm.

Acknowledgments

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THE MERCURY ($^3P_1$) PHOTOSENSITIZED REACTION OF ATOMIC HYDROGEN WITH METHYL CHLORIDE[1]

By G. L. Lee[2] and D. J. Le Roy

Abstract

The method of mercury photosensitization has been used in an investigation of the reaction between atomic hydrogen and methyl chloride at 25°C. The main products are methane, hydrogen chloride, and ethylene chloride. The last is assumed to rise through recombination of chloromethyl radicals formed by either of the reactions,

$$H + CH_3Cl = CH_2Cl + H_2$$
$$\text{or } Hg(^3P_1) + CH_3Cl = CH_2Cl + H + Hg(^1S_0).$$
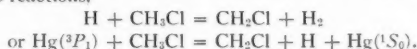
In previous investigations of the reaction between atomic hydrogen and methyl chloride (1, 2, 3) the atoms were produced by the discharge tube method. Boehm and Bonhoeffer found that methyl chloride was decomposed with the liberation of heat. Chadwell and Titani made a study of the products of the reaction and found methane and hydrogen chloride. Cremer, Curry, and Polanyi studied the rate of conversion of para- to ortho-hydrogen in the presence of atomic hydrogen and methyl chloride and concluded, from the independence of this rate on the partial pressure of methyl chloride, that much of the atomic hydrogen was consumed by a wall reaction. Only a small proportion of the apparent decrease in atomic hydrogen could be accounted for by the formation of methane or additional hydrogen, although the accuracy with which they could determine the increase in hydrogen is open to question. They concluded, however, that both of the reactions,

$$H + CH_3Cl = HCl + CH_3 \tag{2}$$
$$\text{and } H + CH_3Cl = H_2 + CH_2Cl \tag{2a}$$
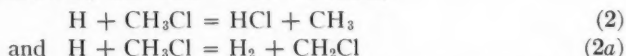
must be slow, corresponding to an activation energy greater than 7.2 kcal. per mole (assuming a steric factor of unity). Although methane formation would, presumably, follow Reaction (2), no products were found which would indicate the occurrence of Reaction (2a). In the present research the method of mercury photosensitization was used to produce atomic hydrogen, and a more detailed investigation of the products was made in an attempt to prove or disprove the occurrence of Reaction (2a).

Experimental

The reaction was studied in both a static and a flow system. In both cases a cylindrical quartz reaction vessel was used, 50 mm. in diameter and 60 mm. long with plane windows. This was placed in a water bath which was maintained at 25°C. A low pressure neon-mercury lamp was used; light from the lamp was admitted to the cell by opening a shutter on the quartz window of the thermostat.

One of the products of the reaction was deposited on the entrance window and the adjacent walls of the cell, with a consequent decrease in the effective intensity of the lamp. This was overcome by measuring the transmitted light with a photoelectric cell placed at the rear quartz window of the thermostat and, by means of a Variac transformer, adjusting the primary voltage of the lamp transformer to keep the intensity of the transmitted light constant.

In the case of the static experiments a few drops of mercury were placed in the bottom of the reaction cell. After the reagents had been admitted, the cell was always left for several hours before illumination, to enable the mercury to reach its saturation pressure. The total volume of the static system was 127 cc. With the circulating system a glass mercury-piston pump with mercury valves was used to circulate the gas through a buffer volume in addition to the reaction cell. The total volume of the circulating system was 265 cc. in experiments C1 and C2, 2450 cc. in experiments C3 to C7. The larger volume made it possible to obtain a greater amount of products for a given percentage change in the composition of the reagents.

The range of methyl chloride pressures used is evident from Table I. The gas was purified by bulb-to-bulb distillation and then condensed into a low temperature fractionating column which was subsequently used in the analysis of the products. It was then taken off at a temperature at which the vapor pressure was 1 mm. or less and measured in a calibrated volume between two mercury columns. Finally, it was condensed into the cell system.

In all experiments the hydrogen pressure was approximately 300 mm. To remove impurities, it was admitted to the cell system through a hot palladium tube while the methyl chloride was frozen out.

With the static system the products of the reaction which were not condensable at the temperature of liquid air were separated from the unconsumed hydrogen by allowing the latter to diffuse through a hot palladium tube mounted on the calibrated receiver of a Toepler pump. Although considerable time and manipulation of mercury levels was required to ensure that all of the hydrogen was removed, it was considered the best method of obtaining an accurate determination of relatively small amounts of methane. The remaining gas, which was shown by combustion to be methane, was measured in a small calibrated volume.

The method of removing hydrogen had to be modified when the circulating system was used, as a result of the large volumes of noncondensable gas involved. In some cases a known fraction of noncondensable gas was analyzed by the procedure used for the static experiments; in others most of the hydrogen was removed directly from the cell system by circulating the gases through a U-tube cooled with liquid air and over the surface of a hot palladium tube. The whole of the methane was then collected as described above.

The gaseous products other than methane and hydrogen were fractionated in the low temperature column (4). The normal take-off pressure for any fraction was in the range 0.5 to 1.0 mm. The same apparatus was used for vapor pressure determinations; the actual pressures were measured on a multiple range McLeod gauge.

Hydrogen chloride was identified both by its vapor pressure and by its complete absorption by moist sodium hydroxide.

Ethylene chloride was identified as one of the products by its vapor pressure, molecular weight, and dew point, and by carbon and chlorine analyses. With the static system the volume of this fraction was of the order of 0.06 cc. of gas at 25°C. and 1 atm. Nevertheless, its vapor pressure over the range $-77°$ to $-50.5°C.$ agreed well with the values obtained with a 0.93 cc. sample from the circulating system, with a 0.09 cc. sample of authentic ethylene chloride, with a large authentic sample (2 cc. of liquid), and with an extrapolation of the data of Pearce and Peters (5). A rather crude determination of the molecular weight was obtained with a small gas density balance; the balancing pressure of 44 mm. corresponded to a molecular weight of 106, compared to the theoretical value of 99. The observed value was sufficiently precise, however, to eliminate mercury dimethyl as a possibility, although the vapor pressure curve for this compound was close to that for ethylene chloride in the temperature range used. The dew point measurements gave vapor pressures of 7.2 cm. and 6.4 cm. at 23.8° and 22.2°C., respectively, for a sample of the product. These values are in reasonable agreement with the interpolated data for pure ethylene chloride (5), viz., 7.4 cm. and 6.9 cm. Two samples of the product were burned with an excess of oxygen over a hot palladium filament in a circulating system; a 1.0 cc. sample gave a carbon number of 1.76, a 1.20 cc. sample gave a carbon number of 1.94. A 2.48 cc. sample of the product when heated with sodium in a closed tube, followed by a chloride determination, gave a chlorine number of 1.7; a more precise determination on a 1.08 cc. sample gave a chlorine number of 1.92. As a result of all these determinations it was concluded that this gaseous product was ethylene chloride.

A further gaseous product was found, having a vapor pressure considerably less than that of ethylene chloride. Although it was shown to contain some chlorine, the small amount formed, about 1% of the methyl chloride consumed, precluded its identification.

The only other product detected was the deposit on the cell walls, referred to previously. It was insoluble in water, ethyl alcohol, acetone, and chloroform but was dissolved by hot nitric acid and by boiling saturated aqueous sodium carbonate solution. A relatively large yield of this product was obtained in a 324 min. experiment using the large circulating system and an original methyl chloride concentration of 4.6%. This was dissolved in boiling sodium carbonate solution. The solution was then acidified with nitric acid and the chloride determined by titration. The amount of chloride found, after allowance was made for the blank, was equivalent to 1.2 cc. of methyl chloride at 25°C. and atmospheric pressure or 0.37 mm. pressure in the cell.

A similar analysis done on the product obtained in experiment C5 gave a chloride content equivalent to 0.13 mm. of methyl chloride. The method of analysis was checked by submitting small samples of pure mercurous chloride to the same treatment. The amount of chloride found agreed with that taken within a few per cent.

The only conclusion that can be drawn from the analysis of the deposit is that it contains chlorine. It cannot even be concluded that all of the chlorine in the deposit was recovered as chloride. Our original assumption that it was mercurous chloride is probably not correct.* The discrepancies in both the carbon and the chlorine balance, particularly at high concentrations of methyl chloride, would suggest that it was an organomercury compound.

The formation of ethylene chloride, presumably by recombination of two chloromethyl radicals, suggested the possibility that ethyl chloride might be formed as well; if this were the case it would probably appear in the methyl chloride fraction. A sample of the initial methyl chloride and two samples of the methyl chloride recovered (both from the same experiment) were analyzed with the mass spectrograph of the Polymer Corporation, Sarnia. The initial methyl chloride analyzed 99.4% methyl chloride, 0.1% methane, 0.2% ethane, 0.1% propylene, 0.2% propane; it was suggested that some of the hydrocarbon traces may have arisen through desorption from the manifold system of the spectrometer. The average analysis of the recovered material was 97.0% methyl chloride, 1.8% hydrogen chloride, 0.9% ethyl chloride, 0.1% methylene chloride, 0.1% propylene, and approximately 0.1% propane. It was suspected at the time that all of the hydrogen chloride was not removed during the fractionation of this particular sample.

Results

The results are shown in Table I; the static experiments are designated by S, the experiments with the circulating system by C. The pressures given are

TABLE I

| Experiment*	Initial			Final			
	H_2 mm.	CH_3Cl mm.	CH_3Cl %	CH_3Cl mm.	CH_4 mm.	HCl mm.	$C_2H_4Cl_2$ mm.
S1	295	2.07	0.70	0.31	1.33	1.16	0.13_1
S2	294	3.07	1.03	1.02	1.27	1.16	—
S3	296	4.46	1.49	2.25	1.07	1.04	0.14_4
S4	291	5.70	1.91	3.43	0.99	1.10	0.20_3
S5	295	7.19	2.38	4.51	1.05	1.20	0.32_8
S6	311	10.62	3.30	7.69	0.93	1.04	0.35_2
C1	313	2.26	0.72	1.32	—	0.72	0.08_8
C2	300	6.88	2.24	4.50	1.22	1.22	0.18_9
C3	296	9.18	3.01	6.16	—	1.33	0.29_1
C4	307	9.15	2.90	6.34	1.39	1.33	0.32_5
C5	299	9.06	2.94	5.83	1.33	1.19	0.33_3
C6	294	8.78	2.90	6.18	1.17	1.32	0.33_4
C7	304	9.00	2.88	6.74	1.08	0.98	0.37_8

NOTE:—*Static and circulating experiments are indicated by S and C, respectively. The lamp was placed closer to the cell for the C runs. Times: S runs, 60 min.; C1, C2, 30 min.; C3 to C7, 324 min.*

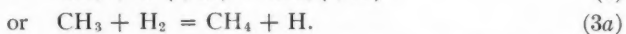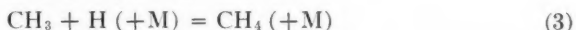*Dr. C. R. Masson, private communication.

those which obtained in the reaction system; they were computed from the volume of the cell system and the pressures and volumes measured in the analytical apparatus.

Discussion

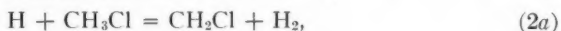The formation of hydrogen chloride is undoubtedly the result of the sequence,

$$Hg(^3P_1) + H_2 = 2H + Hg(^1S_0) \tag{1}$$

$$H + CH_3Cl = HCl + CH_3. \tag{2}$$
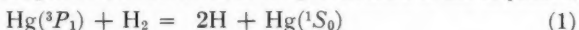
Methane would then be formed by either

$$CH_3 + H (+M) = CH_4 (+M) \tag{3}$$

$$\text{or} \quad CH_3 + H_2 = CH_4 + H. \tag{3a}$$

Ethylene chloride probably arises through recombination of chloromethyl radicals,

$$2CH_2Cl = C_2H_4Cl_2. \tag{4}$$

These radicals could be formed either by a reaction between atomic hydrogen and methyl chloride in competition with (2),

$$H + CH_3Cl = CH_2Cl + H_2, \tag{2a}$$

or by the quenching reaction,

$$Hg(^3P_1) + CH_3Cl = CH_2Cl + H + Hg(^1S_0). \tag{1a}$$
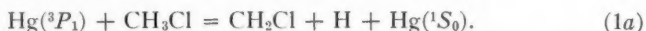
If (1a) were the only reaction leading to the formation of chloromethyl radicals it would be predicted that the ratio of methane or of hydrogen chloride to ethylene chloride would become infinite as the concentration of methyl chloride approached zero.   Fig. 1 suggests that this is not the case.   The least squares line drawn through all the points extrapolates to the value 10.7. The corresponding limiting ratio for $HCl/C_2H_4Cl_2$ is 10.2; that for $CH_4/C_2H_4Cl_2$ is 11.5.   If the average value of 10.7 is taken, the relative rates of (2a) and (2) are given by the expression $k_{2a}/k_2 = 2/10.7 = 0.19$, at 25°C.
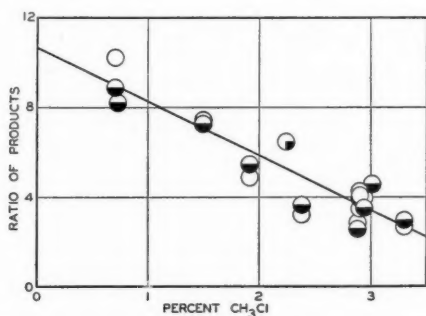

FIG. 1.   ⊙ *Ratio of methane to ethylene chloride,* ◐ *Ratio of hydrogen chloride to ethylene chloride.   The points are for both static and circulating experiments.*

The linear extrapolation of the data of Fig. 1 to zero per cent methyl chloride has been criticised by a reviewer. This criticism is justified, since the assumption of the occurrence or nonoccurrence of Reaction (2a) is based on the validity of this extrapolation. If Reaction (2a) does not occur, then all of the ethylene chloride would, presumably, be formed as a result of Reaction (1a) (followed by (4)), and the ratio

$$\frac{2\ C_2H_4Cl_2}{HCl\ (or\ CH_4)}$$

would approach zero as the concentration of methyl chloride was reduced. Although the accuracy obtainable was not as great as would be desired, the data of Table I show that at the lowest concentrations of methyl chloride there is relatively little carbon or chlorine that cannot be accounted for by Equation (F). At these low concentrations the ratio is, however, appreciably greater than zero, which suggests that Reaction (2a) does actually take place. In view of the questionable validity of extrapolating the data of Fig. 1, the evidence in favor of Reaction (2a) is not conclusive; if it does occur $k_{2a} \geqslant 0.19\ k_2$.

Reaction (2a) cannot, however, account for all of the ethylene chloride formed at finite pressures of methyl chloride. The rapid decrease in the ratio of methane or of hydrogen chloride to ethylene chloride with increasing methyl chloride concentration indicates not only that Reaction (1a) occurs as well, but that methyl chloride has a rather large quenching cross section compared to hydrogen. From Fig. 2 it is seen that the rate of consumption of methyl chloride increases noticeably with methyl chloride concentration, constituting additional evidence for quenching by methyl chloride. Owing to analytical difficulties this curve could not be followed to lower methyl chloride concentrations. The curve of Fig. 2 must, of course, go through the origin. As the concentration of methyl chloride is reduced, the rate of the reaction between atomic hydrogen and methyl chloride will gradually become negligible compared to the rate of recombination of atomic hydrogen, and hence the rate of consumption of methyl chloride will fall off to zero.
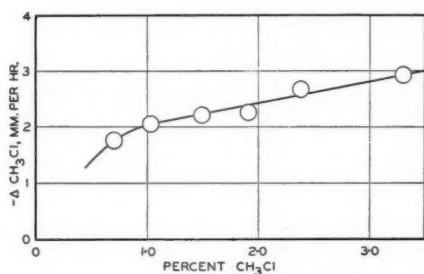

FIG. 2. *Rate of consumption of methyl chloride in the static experiments vs. initial percentage of methyl chloride.*

If R_{1a} represents the rate of Reaction $(1a)$, the rate of consumption of methyl chloride will be given by the expression,

$$R_{CH_3Cl} = R_{1a} + k_2[H][CH_3Cl] + k_{2a}[H][CH_3Cl]. \qquad (A)$$

Also $\qquad R_{CH_4} = k_3[H][CH_3], \qquad (B)$

$$R_{HCl} = k_2[H][CH_3Cl], \qquad (C)$$

and $\qquad R_{C_2H_4Cl_2} = k_4[CH_2Cl]^2. \qquad (D)$

It is immaterial in the present discussion whether methane is formed by Reaction (3) or by Reaction $(3a)$. Assuming steady state concentrations of methyl and chloromethyl radicals,

$$R_{CH_4} = R_{HCl} \qquad (E)$$

and $\qquad R_{CH_3Cl} = R_{HCl} + 2R_{C_2H_4Cl_2}. \qquad (F)$

Equation (F) appears to become valid only at low methyl chloride concentrations. At higher concentrations as much as 30% or more of the methyl chloride consumed cannot be accounted for by the three products, methane hydrogen chloride, and ethylene chloride. We are convinced that ethane is not one of the products. The small amount of ethyl chloride found in the mass spectrographic analysis is probably formed by the reaction,

$$CH_3 + CH_2Cl = C_2H_5Cl. \qquad (5)$$
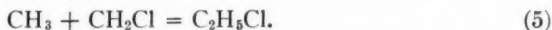
The results of this investigation were disappointing in that it was not possible to obtain unequivocal evidence for or against Reaction $(2a)$. The authors are inclined toward the opinion that it does occur, although the ratio k_{2a}/k_2 obtained by extrapolation in Fig. 1 is not to be taken too seriously. Whether or not Reaction $(2a)$ occurs, it seems necessary to postulate Reaction $(1a)$, although a more appropriate way of studying the latter reaction would be in the absence of hydrogen.

Acknowledgment

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COPOLYMERS OF STYRENE AND CHLORANIL[1]

By J. W. Breitenbach and A. J. Renner

Abstract

The copolymerization of styrene and chloranil in the presence of benzoyl peroxide is described. The molecular weights of the copolymers were determined by osmotic pressure measurements and found to be between 9,000 and 30,000 for the different fractions; their chlorine content is between 37 and 38.2%. The copolymerization occurs with the carbonyl groups of the chloranil, transforming it into a derivative of tetrachlorohydroquinone. This reaction has been verified by degradation of the copolymers with hydrogen bromide.

Introduction

Previous investigations of the copolymerization of styrene and chloranil discovered in 1943 (5, 8) have been mainly concerned with its significance in relation to the theory of retardation (6) and with determining the extent of copolymerization (7). Available information seems to show that such higher molecular weight copolymers are formed by reaction of derivatives of benzoquinone, such as chloranil, bromanil, trichloromethylquinone, 2,6-dichloroquinone, etc. with phenyl substituted vinyl compounds (styrene, anethole, and indene), but not with vinyl chloride or vinyl acetate in the presence of derivates of benzoyl peroxide (o-bromobenzoyl peroxide, etc., but not decalin or tetralinhydroperoxides). The halogen substitution in the quinone seems to be essential for the tendency of copolymerization.

The present paper describes an investigation of the molecular weights and constitution of the styrene–chloranil copolymers.

Breitenbach and Schneider (5) determined the molecular weights of styrene–chloranil copolymers by cryoscopic measurements, but subsequent detailed investigations of the method as applied to lower molecular weight polystyrenes (4) showed that, in spite of good reproducibility, the freezing point depressions are much greater than those corresponding to the true molecular weights. In the present study, therefore, molecular weights were determined by osmotic pressure measurements.

Earlier investigations of the retarding influence of quinones on the polymerization of styrene (3) indicated that chloranil reacted to form an ether of tetrachlorohydroquinone.
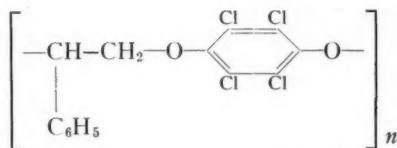
$$\left[-CH-CH_2-O-\underset{\underset{Cl\quad Cl}{}}{\overset{\overset{Cl\quad Cl}{}}{\bigcirc}}-O- \right]_n$$
$$\underset{C_6H_5}{|}$$

Such copolymerization, involving reaction at a carbonyl group, has never been observed elsewhere.   From studies on the chloranil–styrene system, in the presence of benzoyl peroxide, Price (9) concludes that the product is not a copolymer, but has the structure:

$$Cl(CH\!\!-\!\!CH_2)_n\!\!-\!\!\underset{\underset{C_6H_5}{|}}{}$$
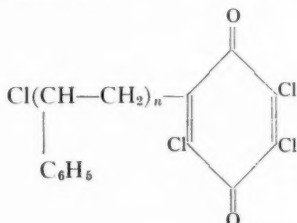
In view of these observations, an experimental investigation has been made of the products of the reaction.

Experimental and Results

Preparation and Fractionation of Copolymers

A mixture of 41.66 gm. (0.401 mole) styrene, 15.01 gm. chloranil (0.161 mole) and 1.23 gm. (0.00423 mole) benzoyl peroxide was heated at 70°C. for 9.75 hr.   During the reaction, the solution was saturated with chloranil, solid chloranil still being present when reaction was complete.   The deep orange-colored solution was poured into ethanol; the product which precipitated was purified by repeatedly (seven times) redissolving it in benzene and reprecipitating with ethanol.   The product retained a pale yellow tint, probably due to traces of chloranil, since Breitenbach and Taglieber (8) have shown that a mixture of styrene, chloranil, and benzoyl peroxide is completely discolored if reaction is continued to complete consumption of the chloranil.   The slightly discolored product was finally accepted, since, in the present studies, it was considered important to obtain a product formed with constant concentration (i.e., excess) of chloranil present, and since small traces of impurities were quite unobjectionable for the purpose at hand (traces of low molecular weight impurities such as chloranil do not influence the osmotic pressure because they can diffuse unrestrained through the membrane).

The reprecipitations yielded 15.45 gm. of product, with a chlorine content* of 37.7%, corresponding to a copolymerization, if it did occur, of 0.041 mole chloranil and nearly 0.05 mole styrene.   Four grams of the product was added to 150 cc. butanone and warmed to 65°C. on the water bath.   Two phases were formed, which were separated by decantation.   The solvent-rich sol phase contained 62.5% of the material, the remainder being present in a highly viscous gel phase.   From the sol phase were obtained two fractions (4 and 5) by precipitation with ethanol.   Three further fractions were ob-

*Analytical determinations were carried out in the microanalytical laboratory of the 1st Chemical Laboratory of the University of Vienna.

tained from the gel phase by dissolving it in benzene and precipitating with ethanol.   In Table I are shown the relative amounts of the fractions obtained, their intrinsic viscosities (in toluene), their chlorine contents, and the calculated mole ratios of chloranil:styrene.

TABLE I

FRACTIONATION OF THE COPOLYMER

Sample	Weight % of original copolymer	Intrinsic viscosity [η] in toluene, conc. gm./l	Chlorine content, %	Mole ratio chloranil/styrene
Copolymer (unfr.)	100	0.0107	37.67	0.80
Fraction 1	6.2	0.0134	38.22	0.84
" 2	9.2	0.0122	—	—
" 3	22.0	0.0116	38.10	0.82
" 4	40.0	0.0095	37.81	0.80
" 5	22.6	0.0070	37.06	0.76

It is interesting to note that, even with constant concentration of chloranil during polymerization, there is a certain distribution of chain-length and styrene–chloranil ratio in the product.   Fractionation occurs not only by molecular size but also by composition, such that the higher molecular weight fractions are enriched in chloranil; this behavior tends to decrease the effectiveness of the fractionation.

Osmotic Pressure Measurements

Osmotic pressure measurements were made in a micro modification of the Schulz–Hellige osmometer constructed from anodically oxidized aluminum. The volume of the osmotic cell was 0.5–0.7 cc., the superficial membrane surface being 3 cm², and the capillary stems of 0.6–0.8 mm. diameter. "Ultracellafilter fein" and "Ultracellafilter feinst", from Membranfiltergesellschaft, Sartoriuswerke, Goettingen, Germany, were used as membrane materials for higher and lower molecular weight fractions respectively.   Measurements were made at 20°C. ± 0.01°.

The equilibrium osmotic head was determined by a semidynamic method. If the level was rising, the osmometer was raised in the solvent bath, while for a falling level, it was lowered.   Equilibrium was assumed to have been attained when the same level was obtained by a rising or falling adjustment, or when constant level was maintained during 24 hr. when reached from only one direction.   The osmotic head was corrected for capillary rise (1.5–1.8 cm. for the capillaries used).

All osmotic measurements were made with redistilled benzene, dried over calcium chloride, as solvent.

In Table II are given the osmotic pressure data for the various fractions. Values of $\lim_{c \to 0} \frac{\pi}{c}$ (column 6) were obtained by graphic extrapolation.

TABLE II

OSMOTIC PRESSURES AND MOLECULAR WEIGHTS OF THE FRACTIONS

Fraction	Conc. gm./l.	Osmotic head, Δh, cm.	Osmotic pressure, $\pi \times 10^3$ atm.	Reduced osm. pr. $\pi/c \times 10^3$ l. atm./gm.	$\lim_{c \to 0} \dfrac{\pi}{c}$	$\overline{M}$
1	2.04	1.98	1.68	0.830	0.81	29,700
	2.40	2.27	2.15	0.845		
	3.12	3.09	2.64	0.845		
3	1.01	1.06	0.905	0.895	0.88	27,300
	2.24	2 48	2.12	0.945		
	5.22	6.05	5.18	0.990		
4	1.08	1.58	1.35	1.25	1.22	19,700
	2.21	3.28	2.80	1.27		
	3.72	5.77	4.94	1.33		
5	1.08	3.40	2.90	2.69	2.64	9,100
	1.52	4.72	4.04	2.68		
	3.80	12.40	10.50	2.79		

The molecular weight of the original polymer, calculated from the molecular weights of the fractions, was found to be 21,000.

The average compositions of the whole polymer and the fractions, calculated from the molecular weights and chlorine analyses, are shown in Table III.

TABLE III

MEAN COMPOSITION OF THE COPOLYMERS

Sample	One mole copolymer contains on the average	
	Moles styrene	Moles chloranil
Unfractionated	70	56
Fraction 1	96	80
" 3	89	73
" 4	65	52
" 5	31	24

These results fully confirm the conclusion of Breitenbach and Schneider (5) that chloranil and styrene in the presence of benzoyl peroxide form copolymers containing many molecules of chloranil chemically bound in one chain. It should be noted, however, that the molecular weights, obtained in the present study from osmotic pressures, are approximately four times the values obtained in the previous investigation by cryoscopic measurements.

Constitution of the Copolymers

Since earlier work (3) indicated that chloranil was bound in the copolymer by an ether linkage, an attempt was made to degrade the polymers with reagents capable of attacking phenol ether bonds. Experiments with hydrobromic acid seemed to be successful.*
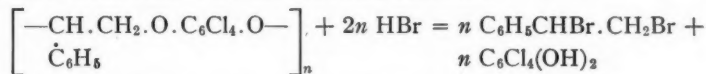
*We are much obliged to Doz. Dr. K. Kratzl for his valuable advice and assistance in the degradation experiments.

When the unfractionated polymer was refluxed with constant boiling (122°C.) aqueous hydrobromic acid, or heated with fuming hydrobromic acid (density = 1.78) in a bomb at 180°C. for 14 hr., only small yields of crystalline degradation products were obtained.   The main products were unidentified resins and oils.   An attempt was therefore made to degrade the polymer in a homogeneous system.   A 4.75 gm. portion of the unfractionated copolymer was dissolved in 75 cc. toluene, warmed at 75°C. and treated for two hours with gaseous hydrogen bromide, purified by paraffin oil and red phosphorus. The cold solution was then saturated with hydrogen bromide again and allowed to stand overnight.   By this treatment, the intrinsic viscosity of the copolymer was reduced from 0.0101 to 0.0032.   Further degradation was not possible by this procedure, but the partially degraded material was found to be soluble in a mixture of 50 cc. glacial acetic acid and 20 cc. benzene, in which medium further degradation with hydrogen bromide was realized.   The benzene and acetic acid were then distilled off, the residue dissolved in ether, the ether solution deacidified with sodium bicarbonate, dried over calcium chloride, filtered, and distilled at reduced pressure (12 mm.).   At 100°C., small amounts of a yellow oil, with an odor resembling that of flowers, distilled over, probably ω-bromostyrene ($C_6H_5.CH=CHBr$).   Between 135° and 145°C., a white crystalline product was obtained which was identified as styrene dibromide, after recrystallizing twice from 80% ethanol.   The melting point was 71.5°C., and it was not depressed by the addition of pure styrene dibromide. Found: C, 36.56; H, 3.15; Br, 60.22%.   Calc.: C, 36.38; H, 3.06; Br, 60.56%.

The residue of the distillation was dissolved in ether and shaken three times with $N/10$ sodium hydroxide.   A small sample of the alkaline solution became deep red with one drop of concentrated nitric acid.   The red color, due to the presence of chloranilic acid, proved the presence of tetrachlorohydroquinone in the residue of the distillation.

The alkaline extract was poured into 50% aqueous acetic acid, the precipitate filtered off, dried, recrystallized from benzene, dried again, and identified as tetrachlorohydroquinone.   The melting point was 233°C., and it was not depressed by the addition of pure tetrachlorohydroquinone.   Found: C, 29.07; H, 0.85; Cl, 56.97%.   Calc.: C, 29.07; H, 0.81; Cl, 57.21%.

The degradation experiments described above prove that phenol ether bonds existed in the original copolymer.   The identified product of the degradation may have been formed by the following reaction:

$$\left[\begin{array}{c} -CH.CH_2.O.C_6Cl_4.O- \\ \dot{C}_6H_5 \end{array} \right]_n + 2n\ HBr = n\ C_6H_5CHBr.CH_2Br + n\ C_6Cl_4(OH)_2$$

Yield of end products: 10% of the initial amount of copolymer.

Copolymers of Styrene and Maleic Anhydride

The remarkable ease with which chloranil forms copolymers suggested that other compounds containing oxo groups might do the same.   For example,

the marked tendency of maleic anhydride to copolymerize has been compared with the retarding effect of quinones (10). Formally, this comparison seems to be admissible by formulating maleic anhydride as a "furoquinone". There is, however, a great difference in behavior of these substances.

A mixture of styrene, maleic anhydride, and benzoyl peroxide (mole ratios 1:0.25:0.001) polymerized at room temperature in 15 hr. to a rigid gel. By heating to 100°C. for a few minutes the gel became a hard mass containing 40% polymer. (Monomer compounds had been removed by extraction with benzene in a Soxhlet apparatus.) The rate of copolymerization was much greater than the rate of polymerization of styrene alone under similar conditions. The mole ratio of styrene: maleic anhydride in the copolymer was 0.74. The copolymer was insoluble in the usual solvents such as benzene, toluene, chloroform, and dioxane, but was soluble in butanone, in which it had an intrinsic viscosity of 0.128. Saponification of the copolymer with 0.5 N potassium hydroxide yielded a polycarbon acid, which was soluble in dioxane ($[\eta] = 0.127$) and in 0.1 N sodium hydroxide ($[\eta] = 0.352$). Apparently, saponification was not accompanied by degradation.

Some data to illustrate the characteristics of the maleic anhydride – styrene copolymerization are given in Table IV. Unlike the copolymerization of chloranil and styrene, the maleic anhydride – styrene reaction does not require initiation by benzoyl peroxide. Comparison with the polymerization of styrene itself indicates that small amounts of maleic anhydride markedly accelerate both the thermal and peroxide initiated polymerizations. Clearly, the behavior of maleic anhydride is only superficially analogous to that of chloranil.

TABLE IV

COPOLYMERIZATION OF STYRENE AND MALEIC ANHYDRIDE
COMPARED WITH THE STYRENE POLYMERIZATION

Moles maleic anhydride/moles styrene	Moles benzoyl peroxide/moles styrene	Temp., °C.	Time, hr.	% Polymerized		Mole ratio maleic anhydride/styrene	$[\eta]$
				Styrene	Maleic anhydride		
0.005	0.0005	50	4	2.54	100	0.2	0.077
—	0.0005	50	4	1.8	—	—	0.18
0.0005	—	90	2	3.0	78	0.15	0.11
—	—	90	2	2.0	—	—	0.20

Discussion

With some knowledge of the composition of the products from the copolymerization of styrene and chloranil, it is possible to draw some conclusions concerning the nature of the reaction involved. The thermal polymerization of styrene, in the absence of benzoyl peroxide initiation, is inhibited by chloranil, with the formation of very short polymer chains. At high concen-

trations of chloranil, two molecules of styrene consume one molecule of chloranil. In the presence of benzoyl peroxide, the copolymers described in the present paper are obtained. Nuclear substituted derivatives of benzoyl peroxide function in a similar manner but if polymerization is initiated by decalinhydroperoxide, tetralinhydroperoxide or *bis*-(α-oxybenzyl)peroxide, retardation results, analogous to that observed in the purely thermal reaction.

It is difficult to reconcile these observations with the commonly accepted mechanism of peroxide initiation of polymerization, a fact that might account for the doubt that has been raised (1) concerning the existence of the copolymers described earlier (5, 7). Prolonged experience and many detailed experiments with these copolymers in this laboratory make it impossible to entertain any such doubts.

The ratio of chloranil to styrene in the copolymer is interesting. At an initial ratio of 0.004 mole chloranil per mole styrene, a copolymer containing 35% chlorine was formed (8). The probability of a chloranil molecule adding to the chloranil end of a growing chain can be taken as zero, since such an addition is not favored energetically. The observed mole ratio of chloranil: styrene of 2:3 in the copolymer indicates that the addition of chloranil to the styrene end of a growing chain is twice as probable as the addition of styrene. This accounts for the great effectiveness of chloranil as a chain terminating agent in the thermal polymerization.

The copolymerization of oxo groups appears not to have been observed with any molecules except the quinones mentioned previously. The reaction of a carbonyl double bond with a growing chain—energetically less favorable than reaction of a carbon–carbon double bond—is possible with the quinones as a result of transition from a quinoid to a benzenoid structure.

A similar phenomenon seems to be the copolymerization of vinyl compounds with oxygen and sulphur dioxide (2).

Price's formulation (9) of the polymers formed of styrene and chloranil in the presence of benzoyl peroxide would appear to be incorrect, since degradation with hydrogen bromide shows the bond between chloranil and styrene to be a carbon–oxygen and not a carbon–carbon bond. Furthermore, the copolymers contain far more chloranil than corresponds to an end group only.

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IONIC SPECIES OF TETRAVALENT URANIUM IN PERCHLORIC AND SULPHURIC ACIDS[1]

By R. H. Betts and Rita M. Leigh

Abstract

A quantitative study of the extraction of tetravalent uranium into benzene by the action of the organic chelating agent thiophenoyl trifluoracetone is described. Data are presented to show that the uranous ion exists mainly in the quadruply charged form in solutions of perchloric acid. It is extracted into benzene as a neutral molecule containing four chelate groups per metal atom. At least two complex species, $U(SO_4)^{++}$ and $U(SO_4)_2$ are present in sulphuric acid solutions. Values of the association constants for the formation of these complex species are given.

Introduction

The configuration and net ionic charge of the tetravalent uranium ion U IV in aqueous solution has been hitherto a matter of speculation in the chemical literature (7, 8, 10). Before dealing with any of the earlier work in detail, it is convenient to consider briefly two main factors which may be expected to influence the structure of such a cation in solution.

The first of these factors is hydrolysis, through which the ionic charge is reduced by elimination of hydrogen ions from the water molecules in the hydration shell of U^{++++}. Such a process will produce $U(OH)^{+3}$, UO^{++}, and $U(OH)_3^+$ etc., if one, two, or three hydrogen ions are removed. For a fixed concentration of acid, the degree of hydrolysis depends in general on the ionic charge and radius of the ion, and tends to be large for an ion with high charge and small radius.

Secondly, the ionic charge may be reduced by the formation of ion-pairs with anions in solution. Considerations of the type described by Bjerrum (4) lead one to expect considerable complexing of this kind for highly charged cations, especially in the presence of bi- or tri-valent anions.

The experimental evidence on the degree of hydrolysis of U IV is inconclusive. Heal (8) has suggested that the configurations $U(OH)^{+3}$ and UO^{++} probably predominate in acid solution, while other workers (7) assumed that UO^{++} is the main species. Kraus and Nelson (10) demonstrated by spectral methods that only two monomeric species, differing by one hydroxyl group, exist in solution down to 0.005 M in hydrogen ion. On the assumption that the main species was U^{++++}, they obtained an equilibrium constant of 0.034 for the equilibrium
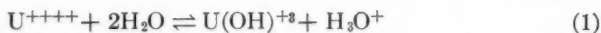
$$U^{++++} + 2H_2O \rightleftharpoons U(OH)^{+3} + H_3O^+ \qquad (1)$$

This value fitted their data over a considerable range of concentrations of U IV and hydrogen ions. However, their data would describe equally well either of the following equilibria:

$$U(OH)^{+3} + H_2O \rightleftharpoons UO^{++} + H_3O^+ \tag{2}$$
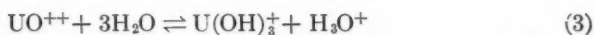
or

$$UO^{++} + 3H_2O \rightleftharpoons U(OH)_3^+ + H_3O^+ \tag{3}$$
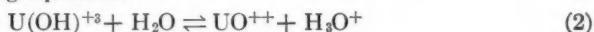
for which the predominant species would be $U(OH)^{+3}$ and UO^{++}, respectively.

At acidities below about 0.05 N, Kraus reported that polymerization reactions occur, leading eventually to precipitation of insoluble products of unknown composition. Since in the present work we do not deal with solutions less than 0.4 M in hydrogen ion, this subject of polymerization will not be discussed further.

Only fragmentary information is available concerning complexes of U IV with inorganic anions. Heal (8), on the basis of polarographic evidence, suggested that U IV forms a complex with sulphate ion; a quantitative interpretation of such data is uncertain, however, because an assumption must be made regarding the formation of complexes of U III with sulphate ion. By assuming that U III forms no complex with sulphate ions, Heal estimated the value of the dissociation constant for the complex U IV sulphate to be about 10^{-3}. However, he did not specify the formula of the complex species.

Some rather indirect evidence is cited by Nichols (11), pointing to the formation of complexes of U IV with both sulphate and chloride ions. He found that these anions catalyzed the auto-oxidation of U IV.
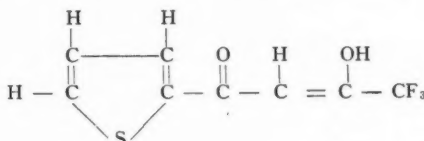
The present work was undertaken to provide unequivocal information on the net charge on the U IV ion in aqueous solution. In addition, data were desired regarding the formation of ion-pairs between U IV and sulphate ion. This anion–cation pair was of particular interest because it has been found recently (2) that small amounts of sulphate catalyze the exchange of uranium atoms between U IV and U VI in perchloric acid. In view of the generally non-complexing properties of the perchlorate ion, this effect points to the formation of complex ions or molecules of U IV and U VI with sulphate. We have shown recently by means of absorption spectra measurements that the higher valence state of uranium is weakly complexed in the presence of sodium sulphate or sulphuric acid, forming UO_2SO_4 with an association constant of 5.0 ± 0.3 (3).

Experimental

A. Theory of the Method

Preliminary experiments showed that while the absorption spectra of U IV in perchloric and sulphuric acids showed some differences, these were not sufficiently great to make the method attractive. The technique finally chosen was that described by Connick and McVey (5, 6) in their studies of the aqueous chemistry of zirconium. These authors have dealt with the theory of the method in great detail, and so only the essential features will be reviewed here.

This method involves the equilibration of an aqueous phase, containing U IV, with benzene, in which is dissolved thiophenoyl trifluoracetone (henceforth denoted as TTA in the text, and referred to as HK in equations). This compound is a weak acid, and forms benzene-soluble chelate compounds with many metallic cations, with the liberation of hydrogen ions. The preparation and properties of TTA have been described by Reid and Calvin (12). Its structural formula is

$$\begin{array}{c} \text{H} \qquad\quad \text{H} \\ | \qquad\qquad | \\ \text{C}\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\text{C} \quad \text{O} \quad \text{H} \quad \text{OH} \\ \parallel \qquad\quad \parallel \qquad\quad | \qquad\quad | \\ \text{H}-\text{C} \qquad\quad \text{C}-\text{C}-\text{C}=\text{C}-\text{CF}_3 \\ \diagdown \qquad \diagup \\ \text{S} \end{array}$$

The acid hydrogen is attached to the oxygen (5, 6). The distribution coefficient $\dfrac{(\text{TTA})_b}{(\text{TTA})_{aq}}$ between 2 M perchloric acid and benzene is 35. Other properties of benzene–water–TTA systems are described by King and Reas (9).

Let us consider, as a specific case, the extraction by TTA of U IV, whose formula we may write as $U(OH)_m^{+4-m}$. It will be assumed, for illustrative purposes, that only one U IV species exists in solution. TTA will be assumed, for the moment, to react with this species according to:

$$U(OH)_m^{+4-m}+ n\,HK \rightleftharpoons UK_n^{+4-n}+(n-m)H^+ + m\,H_2O . \qquad (4)$$
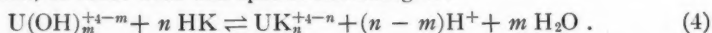
The ratio E of the activity of U IV in the benzene phase at equilibrium to that in the aqueous phase will be called the distribution coefficient, and is given by:

$$\frac{[UK_n^{+4-n}]}{[U(OH)_m^{+4-m}]} = E. \qquad (5)$$

Square brackets will be used to denote activities of the indicated species, and curved brackets to denote concentrations. The equilibrium constant K for Equation (4), at constant activity of water is:

$$\frac{[UK_n^{4-n}]\,[H^+]^{n-m}}{[U(OH)_m^{+4-m}]\,[HK]^n} = K = E.\,\frac{[H^+]^{n-m}}{[HK]^n} . \qquad (6)$$

It follows from Equation (6) that at constant activity of TTA, E will vary inversely with the $(n-m)$th power of the hydrogen ion activity. Also, at constant hydrogen ion activity, E will vary directly with nth power of the activity of TTA. In this simple case, then, one sees how in principle the values of m and n and hence the formulas of the U IV ion and chelate can be deduced.

In practice, however, a number of complicating factors must be taken into account. First of all, we do not know the activity coefficient for many of the species concerned in these equilibria. Connick and McVey give activity coefficients for TTA in benzene up to 0.39 M (5, 6). They also quote unpublished results of W. H. Reas who found that the activity coefficient of the U IV chelate in benzene solution containing TTA is the same as that for TTA itself. No information is available regarding the activity coefficients of U IV salts in

aqueous solutions. In all the experiments described in the present work, the ionic strength was maintained constant by use of sodium perchlorate – per-chloric acid mixtures. It will be assumed therefore that the activity coefficients of all species in the aqueous phase remained constant for all experiments. One may then calculate a distribution coefficient E' in terms of *activities* of the U IV chelate in the benzene phase, and of *concentrations* of U IV in the aqueous phase. It is related to the experimental distribution coefficient E_c, defined in terms of concentrations, by the expression:

$$E' = E_c \cdot \gamma_{TTA}, \tag{7}$$

where γ_{TTA} represents the activity coefficient of TTA, and hence that of the U IV chelate.

A second complication arises from the possibility that some U IV *in the aqueous phase* at equilibrium may be complexed by TTA. Also, more than one species of U IV chelate may exist in the benzene phase. Connick and McVey (5, 6) derived the following relation, which permits experimental investigation of these points:

$$\frac{\partial \ln E'}{\partial \ln[HK]} = -4f_0 - 3f_1 - 2f_2 - f_3 + 4f_0' + 3f_1' + 2f_2' + f_3'. \tag{8}$$

Each f in Equation (8) represents the fraction of the total U IV in the benzene phase having the number of chelate groups denoted by the subscript, and each f' denotes corresponding quantities for the aqueous phase.

A third point to be considered is that several U IV species may coexist in solution. Thus, as indicated earlier, U IV may be U^{++++}, $U(OH)^{+3}$, UO^{++} etc., in equilibrium with one another. Provided that the extractable species is UK_4 (as is shown later) the following relationship exists between E_c and the hydrogen ion concentration, for fixed activity of TTA (5, 6).

$$\frac{\partial \ln E_c}{\partial \ln(H^+)} = -4 + f_1 + 2f_2 + 3f_3. \tag{9}$$

Each f in Equation (9) represents the fraction of the U IV in the aqueous phase having the number of hydroxide groups attached as indicated by the corresponding subscripts. Thus a plot of $\log E_c$ vs. $\log (H^+)$, at constant TTA activity, gives quantitative information regarding the degree of hydrolysis as a function of pH. Actually, to secure measurable extractions, it was necessary to change the concentration of TTA as the pH was changed. Consequently, the results were corrected to unit activity of TTA in the benzene phase by using the formula:

$$E_0 = \frac{E_c \gamma_{UK_4}}{[HK]^4}. \tag{10}$$

This expression arises from the experimental fact (see below) that at constant acidity, E' varies as the fourth power of TTA activity in the benzene phase.

The discussion of the experimental method thus far may be summarized. First, it is necessary to determine what U IV species is extracted into the

organic phase, and whether residual U IV in the aqueous phase is complexed by TTA. This is done by application of Equation (8). Then the variation of E_c with acidity is measured, and corrected to constant TTA activity by Equation (10). From this result, using Equation (9), in which E_0 is substituted for E_c, it is possible to deduce the degree of hydrolysis of U IV as a function of pH.

There remains the application of this method to the problem of ion-pair formation between U IV and sulphate. Clearly, if sulphate or bisulphate ions complex U IV, this will be reflected by a decrease in the extraction of U IV into the organic phase. Whether sulphate or bisulphate ion is the complexing entity is discussed below. The following equation represents this effect (5, 6).

$$\frac{\partial \ln E_0}{\partial \ln(\text{HSO}_4^-)} = -f_1 - 2f_2 - 3f_3 \cdot \cdot \cdot \cdot . \tag{11}$$

This expression relates the variation in the distribution coefficient E_0 to the variation in the concentration of the bisulphate ion at constant hydrogen ion activity. E_0 is the distribution coefficient for U IV, corrected to unit activity of TTA by Equation (10). Each f in Equation (11) represents that fraction of the U IV in the aqueous phase complexed by the number of the sulphate (or bisulphate) groups indicated by the subscript. The slope of the line obtained by plotting $\log E_0$ vs. $\log (\text{HSO}_4^-)$ gives the average number of anions per U IV ion in the complex at any point on the line.

B. Preparation of Materials

Uranous solutions of the desired composition were prepared by reduction of corresponding uranyl solutions at a mercury cathode in a two-compartment cell. Reduction was continued until the first trace of brown U III was formed, which was then removed by blowing air through the solution for several minutes. The uranyl solutions were prepared by dissolving pure uranium trioxide in the appropriate acid.

TTA was prepared for us by Dr. J. Dale of the Defence Research Laboratories in Ottawa, Canada. The properties corresponded closely to those listed by Reid and Calvin (12). Sodium perchlorate was prepared from reagent-grade sodium hydroxide and perchloric acid.

U^{233} used as a tracer in certain of the experiments was prepared from neutron-irradiated thorium, and was purified by accepted methods.

C. Procedure

Solutions of the desired concentration of U IV were pipetted into glass-stoppered cylinders, followed by an equal volume of TTA dissolved in benzene. Generally 2.00 ml. of each phase was used. The flasks were sealed with wax around the stoppers to prevent loss of benzene, and then shaken vigorously until equilibrium was reached. The temperature was maintained at 25.0°C. during this operation. The phases were then separated, centrifuged separately, and analyzed for U IV (see below).

When it was found that the distribution coefficient depended on the fourth power of the TTA activity, precautions were taken to minimize errors arising from uncertainties in this term. The amount of TTA in each flask was determined by weighing the benzene solution added. Also, errors due to losses of solution were avoided by weighing the flasks before and after equilibration. Results for any experiment were rejected when a change in weight of more than 1 mgm. occurred.

The extent of oxidation of U IV to U VI during these operations was investigated, and was found to be negligible in the time taken for the experiment. It was also established that U VI did not extract into the organic phase.

Two methods of analysis were used for U IV. The first of these made use of U^{233} as a radioactive tracer. The preparation and use of this tracer, together with relevant counting techniques, are described elsewhere (1). Aliquots of the separated phases were mounted on 20-mm. watch glasses, and counted sufficiently long to reduce the statistical counting error to less than $\pm 2\%$. Distribution coefficients were calculated from the relative counting rate per milliliter in each phase. Good material balances (in terms of total counts) were obtained by this method. This tracer technique was of particular value when the distribution coefficients were (unavoidably) very low or very high. Wherever possible, however, the distribution coefficients were kept in the neighborhood of unity by suitable choice of the TTA concentration.

In the second method, analysis for U IV in the aqueous phase was made before and after equilibration by measurement of the optical density of the solutions at 650 mμ, with a Beckman Spectrophotometer. (U IV exhibits a strong absorption band at this wave length.) The presence of small amounts of dissolved benzene and TTA in the aqueous phase produced only a negligible error in the optical measurements. The concentration of U IV in the organic phase was calculated by difference from these data.

This method of determining the U IV content of the organic phase by difference is subject to smallest error when the distribution coefficient is near unity. Hence, whenever possible as indicated earlier, the concentration of TTA was chosen accordingly. However, disappearance of U IV from the aqueous phase in any other way except by extraction into the organic solvent would seriously affect the reliability of the method. It is believed that the precautions described above were sufficient to avoid serious errors from this source.

Results and Discussion

1. Effect of TTA Concentration on Distribution Coefficients

The effect of changes in the concentration of TTA on the distribution coefficients is given in Table I and Fig. 1, together with other data. These experiments were made with 1.990 M perchloric acid, 0.0035 M in U IV. The equilibrium concentration of TTA in the organic phase given in column 2 was calculated from the initial concentration in column 1, taking account of the

TABLE I

EFFECT OF CONCENTRATION OF TTA ON EXTRACTION OF U IV AT CONSTANT ACIDITY
$HClO_4 = 1.990\ M$
$U\ IV\ =\ 0.0035\ M$

M TTA, original	M TTA equil.	$\gamma_{TTA} = \gamma_{UK_4}$	Equil. activity TTA, org. phase	E_c	E'
0.0500	0.0478	0.961	0.0460	0.057 ± 0.02	0.055
"	0.0479	"	0.0469	0.049 ± 0.03	0.047
0.0700	0.0660	0.947	0.0625	0.167 ± 0.05	0.158
0.0900	0.0836	0.937	0.0783	0.434 ± 0.01	0.407
0.1000*	0.0904	0.933	0.0843	0.710 ± 0.03	0.662
0.1000	0.0914	0.932	0.0852	**0.758 ± 0.01	0.706
"	0.0914	0.932	0.0852	0.737 ± 0.02	0.687
"	0.0920	0.932	0.0857	**0.712	0.664
"	0.0915	0.932	0.0853	0.698 ± 0.18	0.651
0.1250	0.1131	0.919	0.1039	1.51 ± 0.3	1.39
0.1500	0.1357	0.910	0.1235	2.66 ± 0.04	2.42
0.2000	0.1823	0.891	0.1624	6.86 ± 0.15	6.11
0.2500	0.2300	0.876	0.2015	14.2 ± 2.0	12.4

* 2.20 ml. used in aqueous phase. All distribution coefficients in this table, except for two marked (**), were measured using U^{233} as tracer.
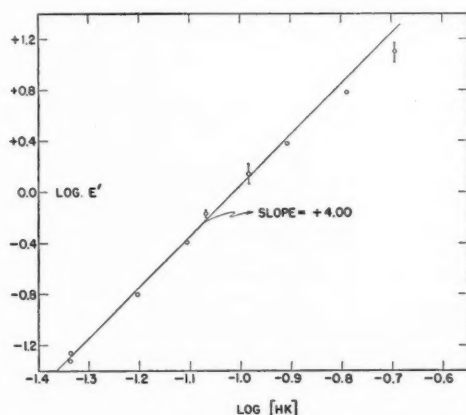

FIG. 1.   Effect of concentration of TTA on distribution coefficient of U IV at constant acidity.

amount used up in complex formation with U IV, and a distribution coefficient of 35 for the residual TTA. Values for the activity coefficient γ of TTA given in this and other tables were obtained by interpolation of Connick's data (5, 6). The experimental distribution coefficients E_c are given in column 5, with average deviations for two to four determinations. Values of E' in column 6 were calculated from E_c, using Equation (7). Corresponding values of log E' and log [TTA] are plotted in Fig. 1. A line of slope +4 is indicated in this figure. It is clear from this value of the slope that U IV extracts into the organic phase only as UK₄, i.e., all the f's in Equation (8) are zero, and all the f terms are

zero except f_0', which has a value of one. Further, complexing of the residual U IV in the aqueous phase is unimportant until the equilibrium activity of TTA in the benzene exceeds 0.12. Some complexing may occur at higher concentration of TTA as indicated by the deviation of the last two points from the line of slope $+4$.

2. Effect of Hydrogen Ion Concentration on Distribution Coefficients

The results for experiments in which the hydrogen ion concentration in the aqueous phase was varied are given in Table II. The concentration of perchloric acid + sodium perchlorate was constant at 1.990 M in these experiments. The first five column headings in Table II have the same significance as in Table I. E_0 in column 6 was calculated from E_c, using Equation (10). E_0 represents the value of the distribution coefficient for unit activity of TTA in the organic phase, and is expressed in terms of activity of UK_4 in the benzene and concentration of U IV in the aqueous phase. Corresponding values for the concentration of hydrogen ion are given in the last column. Values of $\log E_0$

TABLE II

EFFECT OF CONCENTRATION OF HYDROGEN ION ON EXTRACTION OF U IV WITH TTA
$(NaClO_4) + (HClO_4) = 1.990 \ M.$ U IV = 0.0035 M.

M TTA, orig.	M TTA	$\gamma_{TTA} = \gamma_{UK_4}$	Equil. activity TTA, org. phase	E_c	E_0	(H+)
0.1000	0.0904*	0.933	0.0843	0.71**	$1.31.10^4$	1.990
"	0.0914	0.932	0.0852	0.74	$1.31.10^4$	"
"	0.0913	"	0.0851	0.77	$1.37.10^4$	"
"	0.0914	"	0.0852	0.74	$1.31.10^4$	"
"	0.0920	"	0.0857	0.71	$1.23.10^4$	"
"	0.0897	0.933	0.0837	1.22	$2.32.10^4$	1.73
"	0.0896	"	0.0836	1.27	$2.42.10^4$	"
"	0.0895	"	0.0835	1.29	$2.47.10^4$	"
0.0500	0.0462	0.963	0.0445	0.22	$5.40.10^4$	1.526
0.1000	0.0886	0.933	0.0827	1.73	$3.45.10^4$	"
"	0.0892	"	0.0832	1.43	$2.78.10^4$	"
0.0500	0.0547	0.963	0.0440	0.28	$7.19.10^4$	1.296
0.0667	0.0598	0.952	0.0569	0.58	$5.27.10^4$	"
0.0833	0.0729	0.943	0.0687	1.47	$6.22.10^4$	"
0.0500	0.0436	0.964	0.0420	0.58	$1.80.10^5$	1.054
0.0667	0.0573	0.954	0.0547	1.20	$1.28.10^5$	"
0.0250	0.0235	0.983	0.0231	0.050**	$1.74.10^5$	"
0.0500	0.0419	0.966	0.0405	0.97	$3.48.10^5$	0.835
"	0.0415	0.965	0.0400	1.08	$4.07.10^5$	"
"	0.0418	0.965	0.0403	0.99	$3.62.10^5$	"
0.0250	0.0228	0.983	0.0224	0.106**	$4.15.10^5$	"
0.0500	0.0389	0.966	0.0376	2.52	$1.22.10^6$	0.598
"	0.0384	"	0.0371	3.18	$1.62.10^6$	"
"	0.0384	"	"	2.84	$1.45.10^6$	"
"	0.0382	0.967	0.0369	2.97	$1.55.10^6$	"
0.0333	0.0230	0.983	0.0226	2.18	$8.21.10^6$	0.358
"	0.0236	"	0.0232	1.79	$6.07.10^6$	"

* 2.20 ml. in aqueous phase.   All E_0 values except those marked (**) determined by spectrophotometer.
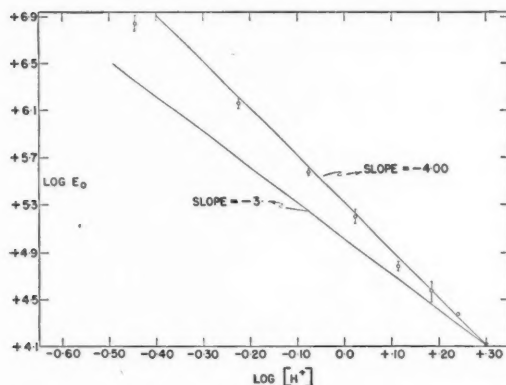
FIG. 2. *Effect of hydrogen ion on the distribution coefficient of U IV at constant activity of TTA.*

and log (H^+) are plotted in Fig. 2. The average deviations in the values of log E_0, for fixed concentration of hydrogen ion, are indicated by vertical bars in Fig. 2.

A line of slope -4 is drawn through the experimental points in Fig. 2. Reference to Equation (9), in which E_0 is substituted for E_c, indicates that all the f terms must be negligibly small or zero in order that a slope of -4 can be obtained. This means that the predominant species of U IV in aqueous perchloric acid is U^{++++}. If the main species were $U(OH)^{+3}$, a slope of -3 would be observed in this plot. Such a slope is also indicated in Fig. 2. Clearly, this result decides unequivocally in favor of U^{++++} as the formula of U IV in solutions of perchloric acid.

3. Effect of Bisulphate Ion Concentration on Distribution Coefficients

Results for experiments in which the concentration of bisulphate ion was varied from 0.0 M to 0.0925 M are given in Table III. The concentration of

TABLE III

EFFECT OF BISULFATE ION CONCENTRATION ON EXTRACTION OF U IV

M TTA, orig.	Equil. conc. of TTA	$\gamma_{UK_4} = \gamma_{TTA}$	Equil. activity of TTA	E_c	E_0	(HSO_4^-)
0.1000	0.0920	0.932	0.0857	0.712	$1.23.10^4$	0.0
"	0.0924	0.931	0.0860	0.601	$1.02.10^4$	0.00183
"	0.0930	0.931	0.0866	0.495	$8.20.10^3$	0.00459
"	0.0939	0.930	0.0873	0.366	$5.87.10^3$	0.00918
"	0.0949	0.930	0.0883	0.228	$3.49.10^3$	0.01835
"	0.0961	0.930	0.0894	0.089	$1.30.10^3$	0.0459
0.2000	0.1876	0.889	0.1668	1.04	$1.34.10^3$	0.0459
"	0.1904	0.888	0.1692	0.484	$5.28.10^2$	0.0925

hydrogen ion was 1.990 M in all these experiments. Sulphuric acid has been considered to be a monobasic acid in view of the weakness of its second dissociation. The concentration of U IV was 0.00325 M. Corresponding values of log E_0 and log (HSO_4^-) are plotted in Fig. 3. It should be pointed out that the values of (HSO_4^-) in Table III and Fig. 3 are not equilibrium values, but represent the total concentration of bisulphate ion, including that part bound up in complexes with U IV.
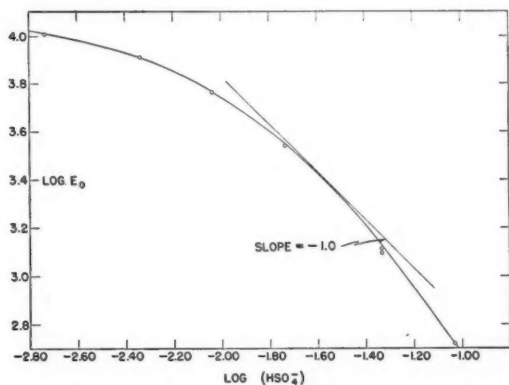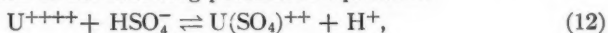

FIG. 3. *Effect of bisulphate ion concentration on distribution coefficient of U IV at constant acidity.*

If only one complex of U IV and bisulphate ion existed in solution, i.e. USO_4^{++}, the slope of the curve in Fig. 3 would be between 0 and a limit of -1 [see Equation (11)]. This value for the limiting slope is shown in Fig. 3. It is clear that at moderate concentrations of bisulphate, complexes containing at least two sulphate (or bisulphate) groups must exist in solution.

Values for the association constants may be calculated from the data in Table III on the basis of the following postulated equilibria:

$$U^{++++} + HSO_4^- \rightleftharpoons U(SO_4)^{++} + H^+, \qquad (12)$$

$$K_1 = \frac{(U(SO_4)^{++})\,(H^+)}{(U^{++++})\,(HSO_4^-)} \qquad (13)$$

and
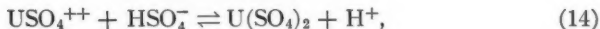
$$USO_4^{++} + HSO_4^- \rightleftharpoons U(SO_4)_2 + H^+, \qquad (14)$$

$$K_2 = \frac{(U(SO_4)_2)\,(H^+)}{(U(SO_4)^{++})\,(HSO_4^-)}. \qquad (15)$$

These equilibria represent the simplest complexes which may be formed between one uranous ion and one or two bisulphate ions. The association constants are expressed in terms of concentrations, since it is believed that the (unknown) activity coefficients of the species did not change significantly over the small variations in the ionic environment employed in these studies. The

justification for assuming these complexes to be $U(SO_4)^{++}$ and $U(SO_4)_2$ rather than $U(SO_4)H^{+++}$ and $U(SO_4)_2H^+$ respectively lies in the fact that the first hydrogen ion is strong in sulphuric acid. When this ion is replaced by a more highly charged entity like U^{++++}, the remaining hydrogen should show at least as great a tendency to ionize as the first one did. This expectation has been proved experimentally in the case of the U VI complex in solution; the complex species in this case is UO_2SO_4 rather than $UO_2(SO_4)H^+$ (3).

The quantitative relation between the activity of UK_4 in the benzene phase and the concentration of uncomplexed U^{++++} in the aqueous phase in 1.99 M perchloric acid is given in Table III:

$$\frac{[UK_4]}{(U^{++++})} = 1.23 \times 10^4. \qquad (16)$$

In the presence of bisulphate, E_0 is given by:

$$E_0 = \frac{[UK_4]}{(U^{+4}) + (U(SO_4)^{++}) + (U(SO_4)_2)} . \qquad (17)$$

Equations (13), (15), and (16) may be solved for $(U(SO_4)^{++})$, $(U(SO_4)_2)$, and $[UK_4]$ respectively, and these values substituted in Equation (17), leading to:

$$E_0 = \frac{1.23 \times 10^4}{1 + \dfrac{K_1(HSO_4^-)}{(H^+)} + \dfrac{K_1K_2(HSO_4^-)^2}{(H^+)^2}} . \qquad (18)$$

Since all solutions used were 1.99 M in hydrogen ion, for convenience we substitute K_3 and K_4 for $\dfrac{K_1}{(H^+)}$ and $\dfrac{K_2}{(H^+)}$ respectively, with the result that

$$E_0 = \frac{1.23 \times 10^4}{1 + K_3(HSO_4^-) + K_3K_4(HSO_4^-)^2} . \qquad (19)$$

Substitution in Equation (19) of appropriate experimental values of E_0 and (HSO_4^-) from the last two experiments in Table III gave values for K_3 and K_4 of 173 and 0.43 respectively. These values were then corrected by successive approximations, taking into account that the equilibrium concentrations of bisulphate ion differ slightly from the stoichiometric concentrations, leading to values for K_3 and K_4 of 180 and 0.40, respectively.

These calculations for K_3 and K_4 were repeated, using other combinations of E_0 and (HSO_4^-) values from Table III, and gave somewhat lower results, the average of all values being 168 ± 12 and 0.37 ± 0.03. The hydrogen ion independent association constants defined by Equations (13) and (15) are 338 ± 24 and 0.74 ± 0.06, respectively.

Acknowledgment

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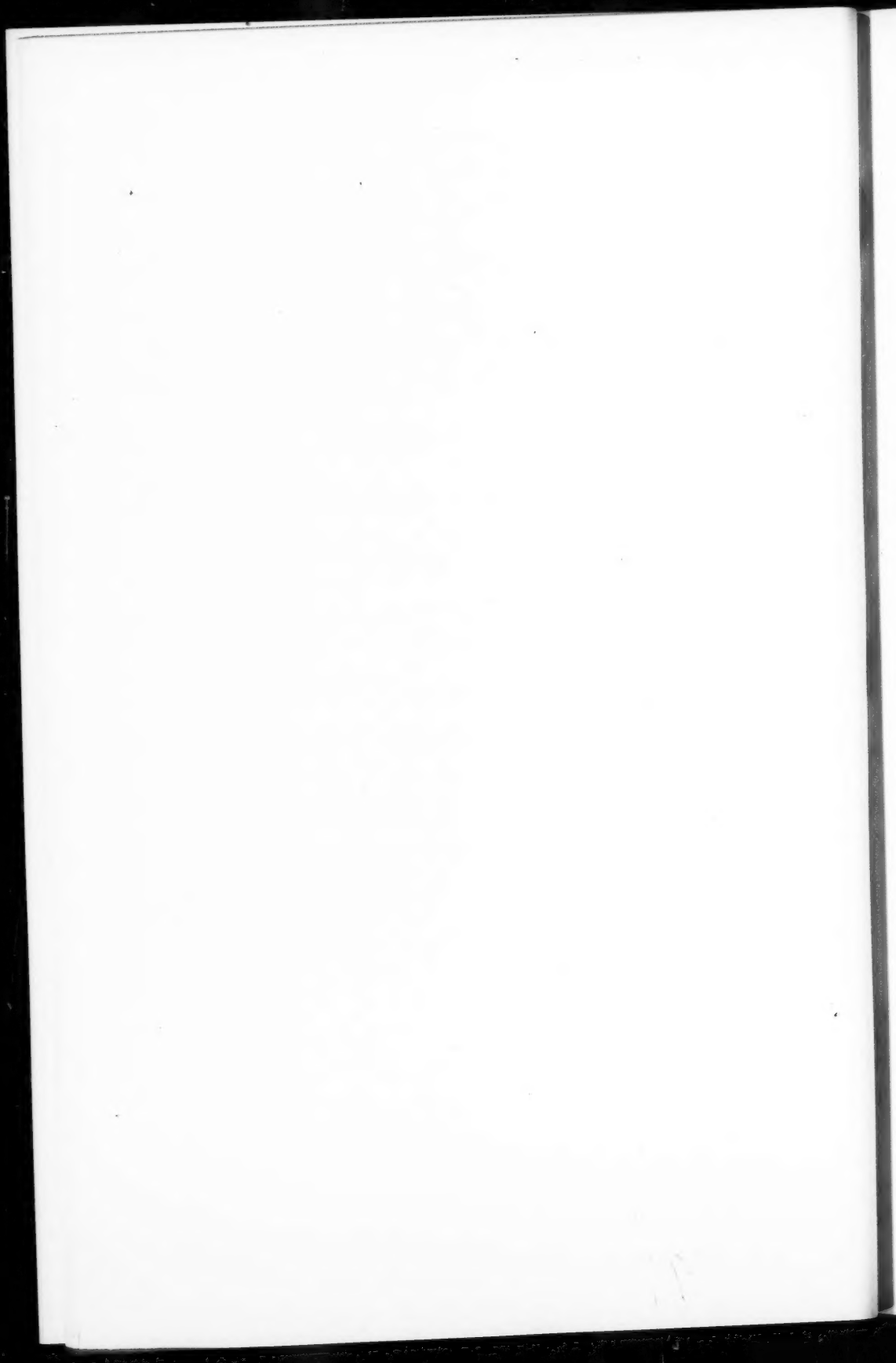
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